AGRICULTURAL RESEARCH INSTITUTE

PUSA

PROCEEDINGS

OF THE

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SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
PHYSICAL CHARACTER.

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PROCEEDINGS OF

THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

Address of the President, Sir Archibald Geikie, K.C.B., at the Anniversary Meeting on November 30, 1912.

In reviewing the progress of the Royal Society since St. Andrew's Day last year we have first to take note of the losses which during the interval have been inflicted on our ranks by the hand of death. Though, perhaps, somewhat fewer in number than the average of recent years, these losses have included some of our most distinguished associates. Four of our Foreign Members have passed away, and on our Home List we have to regret the death of twelve Fellows, among whom are two former Presidents of the Society and Copley Medallists. While both the biological and the physical sides of science have shared in this bereavement, it is more especially on the former and particularly on the domain of botany that the losses have fallen.

Two of our recently deceased Foreign Members were eminent representatives of botanical science. JEAN B. ÉDOUARD BORNET, who was elected into our number only two years ago, died at the end of last year at the ripe age of 83, having attained the highest distinction by his investigations into the structure and life-history of the Algæ.

EDUARD STRASBURGER, one of the most original and versatile botanists of his day, died last May, in his 70th year. The brilliance of his researches in various departments of botany, more particularly in cytology and plant anatomy, placed him in the front rank of the science, and drew around him, in his laboratory at Bonn, students from all parts of the world.

In FERDINAND ZIRKEL mineralogy, geology, and petrography have lost one of their foremost exponents, and his wide circle of friends mourns

the death of a loyal and lovable man. We had hoped that he would attend the Society's Anniversary celebration last July. He wrote, not uncheerfully, that he would gladly have come to London had the state of his health permitted, but he passed away on June 11. He was the first man of science on the Continent who realised the far-reaching importance of the work of our late distinguished Fellow, Henry Clifton Sorby, in the application of the microscope to the solution of the many problems presented by the composition and intimate structure of the rocks that form the crust of the earth. ZIRKEL'S name will always stand associated with Sorby's in the forefront of the pioneers who led the way in the transformation or re-creation of the science of petrography. His own original contributions to this science were marked by their singular grasp and lucidity, while his massive 'Lehrbuch der Petrographie' remains as a classic monument of his industry, his wide acquaintance with the literature of his subject in every language, and his admirably clear and orderly method of presentation. He was elected one of our Foreign Members in 1897—an honour which he keenly appreciated.

By the death of JULES HENRI POINCARÉ at the comparatively early age of 58, mathematical science has lost one of its most distinguished cultivators. He had already come to the front as a discoverer in the domain of pure analysis, when his accession to a Chair of Mathematical Physics turned his attention towards the great concrete realm of natural philosophy. This branch of knowledge he expounded from the mathematical outlook in a series of memoirs and treatises which established for him a new reputation. His profound and highly trained mathematical intuition enabled him, in not a few cases, to give a fresh impetus to problems that were pending and for the time at a standstill, such, for example, as the question of the classification of the various forms possible for a self-gravitating rotating planet, on which Lord Kelvin shed much fascinating light without entirely unravelling it. POINCARÉ'S work on celestial mechanics, culminating in a formal treatise on that subject, is a masterly and illuminating attempt to bring the empirical and tentative solutions, which have proved to be adequate for practical calculations, within the domain of precision which belongs to the modern theory of expansions in series. In the more complex physical subjects, such as thermodynamics and the theory of electricity, where mathematical reasoning has to be largely of tentative and inductive type, he was a keen student and a candid critic. His wide studies in these fields afforded ample material for the philosophic workings of a mind interested, like those of many of the greatest mathematical discoverers, in probing the ultimate foundations of knowledge; and the popular essays in which he gave rein to his criticism

and often to his fancy, always in exquisite literary form, brought him a seat in the French Academy and made his name familiar in wide circles which his constructive work could hardly have reached.

In HENRI POINCARÉ we lose a colleague who had long been in intimate and cordial relations with his fellow workers in this country. His name stands first in the awards of the Sylvester Medal; he was a Medallist of the Royal Astronomical Society; and at the time of his decease his nomination was ripening for the chief award of the Royal Society—the Copley Medal. Illness prevented him from attending our Anniversary Celebration last July; we had heard that his health was improving, but on the last day of our festival news came from Paris of his sudden death. In obedience to a widely-expressed desire our Secretary, Sir Joseph Larmor, and the Astronomer Royal were deputed to represent the Royal Society at his funeral.

By the death of SIR JOSEPH DALTON HOOKER the Royal Society has been deprived of its oldest member, its most distinguished botanist, one of its long line of Presidents, and one to whom it had awarded all the honours which it could bestow. Born as far back as the year 1817, this great man began his illustrious career, at the early age of 22, by accompanying Sir James Clark Ross in the famous expedition of the "Erebus" and "Terror" to the Antarctic regions in 1839. The publication of the results of this voyage in his 'Flora Antarctica' placed HOOKER at one bound in the first rank of the systematic botanists of the day. Thenceforward he continued to enrich science with contributions marked at once by great originality and philosophical insight. His keen interest in the problems of the geographical distribution of plants, and his ardent enthusiasm as an explorer of the botany of new or little known regions, combined to make him one of the most intrepid and accomplished travellers of his time. His Antarctic experiences were followed before many years by his memorable journeys in the Himalayas, Tibet, Nepal, and Sikkim, from which he returned with so rich a harvest of important observations. In later years he visited Palestine and brought back results interesting alike to the botanist and the geologist, explored the Atlas and the uplands of Morocco, and, eventually extending his surveys into the New World, traversed the Rocky Mountains in Colorado and Utah.

Sir Joseph's association with Charles Darwin and the publication of the 'Origin of Species' is a memorable incident in the history of modern science. In recognition of the great value of his early botanical researches HOOKER was elected into the Royal Society in 1847 at the age of 30. Seven years later further approbation of his work was marked by the award of a

Royal Medal in 1854. His genial character, his judicious temperament, and his business capacity, led to his being frequently chosen to serve on the Society's Council. He repeatedly filled the office of Vice-President, and he occupied the Presidential Chair for five years, from 1873 to 1878. The crowning honour of the Copley Medal was conferred upon him in 1887, when he had reached his 70th year; and a few years later, when the Darwin Medal had been instituted, it was awarded to him in recognition of his association with the great naturalist whose name it bears. Universally acknowledged to stand at the head of the botanists of his day, continuing to work at his favourite studies up to the very end of his long and brilliant career, beloved by all who knew him, and full of honours as of years, he passed to his rest on December 10, 1911, in the 94th year of his age.

In LORD LISTER we have lost one of the most epoch-marking men of our time. By patient and skilful investigations along a strictly scientific path, his intuitive genius enabled him eventually to transform the art of the surgeon, and thereby to lay mankind under an eternal debt of gratitude for his achievement in the lessening of mortality, the diminution of suffering, and the extension of successful surgical treatment to operations which were previously considered too dangerous to be undertaken. Few chapters in the history of the advance of experimental science are more fascinating than those which, in Lister's published papers and in other publications, trace the long and laborious investigation, the difficulties and disappointments which accompanied it, and the opposition or indifference with which it was watched outside, before he emerged in triumph with his purpose accomplished. At the beginning of his career, his kindly nature was shocked at the appalling mortality in the surgical hospitals with which he was acquainted, and, as he felt sure that some remedy might be found, he set himself deliberately to seek for it. Convinced of the truth of Pasteur's researches in regard to the origin of putrefactive changes, he conceived that if he could exclude or destroy the micro-organisms everywhere present surgical wounds would probably heal, and the pain and fatal results accompanying them would be diminished or even prevented. Step by step, as his knowledge of this obscure subject widened, his methods were altered, improved, and simplified, until their undoubted success compelled the attention of the medical world. His antiseptic treatment was, ere long, adopted in hospital after hospital with ever-increasing appreciation, until it is now in universal use all over the world.

LISTER was himself a skilful surgeon, and as a man of science he made important contributions to surgery and medicine. In particular, his suggestive work in regard to bacteria was largely instrumental in founding

the important modern science of bacteriology. But, undoubtedly, the achievement which will hand his name down to the remotest posterity has been the creation of aseptic surgery. The remarkable company of eminent and representative men who from all parts of the civilised world gathered round his bier in Westminster Abbey was a visible expression of the gratitude of all countries for his priceless services.

The value of LORD LISTER'S early contributions to science was recognised by the Royal Society, which elected him a Fellow in 1860, when he was 33 years of age. After he left the professorship which he held in the University of Edinburgh and had settled in London, he served frequently on the Council of the Society. He was Foreign Secretary from 1893 to 1895, and he filled the Presidential Chair from 1895 to 1900. He received a Royal Medal in 1880, and was awarded the Copley Medal in 1902. His kindliness and courtesy, his simplicity and modesty, endeared him to a wide circle of friends who warmly cherish his memory. He died at Walmer on February 10 last, in the 85th year of his age. There was a widespread desire that his remains should be laid in Westminster Abbey, but by his own direction he was buried beside his wife in the West Hampstead Cemetery.

From among the chemists on our List of Fellows we have lost during the past year DR. EDWARD DIVERS and DR. HUMPHREY OWEN JONES. DR. DIVERS spent his earlier years in this country; but having been induced in 1873 to accept the offer of a Professorship of Chemistry from the Government of Japan, he remained on active service in that country for twenty-six years. On his return to England his long experience found useful employment in the councils of learned societies and other institutions. He became a Fellow of the Royal Society in 1885. He died in April last, in his 75th year.

By the sudden and tragic death of DR. JONES and his young bride in the Alps last summer, science has been deprived of one who, though only 34 years of age, had already distinguished himself as an original observer and an excellent teacher, and who would doubtless soon have risen to eminence among the chemists of his day. His merits were recognised when he was elected into the Royal Society this year. We lament that a career so full of promise should have been so suddenly cut short by an accident met with in a recreation in which he was one of the most noted leaders.

The representation of Engineering in our Fellowship has been diminished since our last Anniversary by the death of HENRY TAYLOR BOVEY. Born in 1850, he became 12th Wrangler at Cambridge in 1873, and after engaging in various engineering works accepted in 1877 the Chair of Engineering at McGill University, Montreal. His skill and energy transformed the teaching of applied science in that institution and made the College the most important

engineering school on the American continent. In 1908 he was induced to return to England and to accept the rectorship of the Imperial College of Science and Technology in London. Owing to failing health, however, he resigned that appointment at the end of the following year. He died on February 2 last.

The late Major-General EDWARD ROBERT FESTING connected the Royal Society with the Royal Engineers. In association with Sir William Abney he communicated papers to the Society on a variety of physical subjects, especially on photometry. He was elected a Fellow in 1886.

For many years Admiral SIR JOHN DALRYMPLE HAY, Bart., was one of the most regular attendants at the meetings of the Society. He was born in 1821, entered the Navy at the age of 13, and had a varied and interesting career until he retired from active service afloat in 1859. He had early shown an interest in some branches of science, particularly in meteorology, and after he retired from the sea he had opportunities of advocating the application of science to the needs of the Navy. In 1861 he was appointed Chairman of the Iron-plate Committee that was formed for the purpose of carrying on experiments on the application of armour to the sides of vessels of war. In 1864 he was elected a Fellow of the Royal Society. His reminiscences of his experience in the Navy and in official life, his exceptional descriptive faculty, his dignified presence and old-time courtesy and his keen sense of humour made him a special favourite in society. He passed away on January 28 last, in the 91st year of his age.

In OSBORNE REYNOLDS we have lost one of our leading physicists and scientific engineers. His original contributions to the kinetic theory of gases and the molecular theory of viscosity, those on the flow of liquids in channels, and on the determination of the mechanical equivalent of heat, have given him an assured place in the history of physical science. His labours as a University Professor have brilliantly illustrated the intimate connexion which exists between physical experiment and practical engineering progress, and have endeared him to the wide circle of pupils who studied under him. He was elected one of our Fellows in 1877 and was awarded a Royal Medal in 1888.

Dr. RAMSAY HEATLEY TRAQUAIR, who has just died at Edinburgh in his 72nd year, has long held a foremost place in the ranks of vertebrate palæontologists. His medical training, and his early devotion to the study of the anatomy of fishes, gave him a grasp of the ichthyology of past time such as few of his contemporaries could equal. By concentrating his attention on the fossil fishes of the Old Red Sandstone and the Carboniferous system, he was enabled to throw much new light on the relations of these

organisms to each other, while at the same time he showed how their specific forms could be utilised for the determination of problems in stratigraphy. He joined the Royal Society in 1881, and in 1907 received one of our Royal Medals.

Dr. JOHN WILLIAM MALLET, who was elected into the Society in 1877, was the son of Robert Mallet, one of the pioneers of modern seismology. He graduated in medicine, but specially interested himself in chemical studies. Settling in the United States, he became a Fellow of the College of Physicians of Philadelphia, and was Professor of Chemistry in the University of Virginia. But he retained his connection with this country, and in 1906 was one of the representatives of the Royal Society at the celebration of the 200th anniversary of the birth of Benjamin Franklin at Philadelphia.

ROBERT HOLFORD BOSANQUET was for some time a Fellow of St. John's College, Cambridge. His investigations in the theory of sound, especially in relation to music, attracted attention 20 years ago. He became a Fellow of the Royal Society in 1890.

The Report of the Council, now in the hands of the Fellows, presents a brief summary of the operations of the Society during the past year. Among these, the most prominent incident has been the celebration of the 250th Anniversary of the foundation of the Society. The programme of proceedings, which had been drawn up after much careful deliberation, was carried out in detail as arranged, and with a success on which, I think, the Society may well be congratulated. Our invitation was responded to by nearly all the Universities and the chief learned Societies, both in the Old and in the New World. These different institutions were, in almost all cases, personally represented by delegates, though a few forwarded by post their addresses of felicitation. Never before in our history did so numerous a company of representatives of learning and science assemble under our roof. No more striking evidence could have been given of the sympathy which draws together the students of natural knowledge, and unites them into a world-wide brotherhood, inspired by one common spirit of devotion to the study of nature and the search after truth. Nor could a more gratifying tribute have been offered to the Royal Society, in recognition of the part which it has played in the development of science during its career of two and a half centuries, than the addresses which were presented to us in our Library on July 16 last. These documents form a united and impressive testimonial which the Society will preserve with pride through the years to come. Since the Delegates returned to their homes, I have received many letters from them expressive of their great appreciation of the pleasure

which they had received, and their warm congratulations on the success of our Celebration.

As a permanent memorial of this interesting event in the history of the Society, the President and Council determined last year to begin the preparation of a volume containing a facsimile reproduction of the signatures in the first Journal-book and in the Charter-book from the year 1660 down to the present time. As a series of the autographs of the most eminent men of science and learning who have lived during the last 250 years, this collection has probably no rival in the world. The volume, which has been admirably produced at the Oxford University Press, was completed in good time before the advent of the Anniversary celebration. A copy was at once presented to the Patron of the Society, His Majesty the King, who was pleased to express his appreciation of this interesting memorial. A volume embracing nearly 100 folio plates and a complete index to the signatures is necessarily costly. But in order that it may come into the possession of those who are most directly interested in its contents, the Council has ordered that each Fellow of the Society may obtain a copy at one-third of the published price.

Another volume has concomitantly been prepared and published, in the form of a new, considerably expanded, and thoroughly revised edition of the 'Record of the Royal Society.' Containing a brief history of the Society, with an account of its Charters, Statutes, and organisation, lists of its Fellows and Officers from the beginning, its Medallists and Lecturers, its portraits, relics, and other property, the book forms a useful compendium of information regarding the Society. It is embellished with twenty plates showing views of the successive apartments occupied by the Society since its foundation, and including also portraits of former Presidents and others. This volume is also obtainable by the Fellows at one-third of the published price.

MEDALLISTS, 1912.

The Copley Medal.

The Copley Medal is this year assigned to Prof. Felix Klein, of Göttingen, for his researches in mathematics.

Prof. Klein is, perhaps, most widely known in this country for his investigations in geometry, which attached themselves closely to the work of Cayley and other British mathematicians. This work has expanded and systematised our conceptions of non-Euclidean geometry, and indeed the philosophy of geometry in general.

Of at least equal importance have been his researches in the theory of functions. In his earlier papers he dealt mainly with the transformation of elliptic functions and the related theory of modular functions. The key to the most of what followed lies in the memoir, 'Neue Beiträge zur Riemannischen Functionentheorie,' published in 1882. In this memoir, quite independently of Poincaré, and from an entirely different point of view, Klein lays the foundations of the theory of automorphic functions. He here considers for the first time the relations between an infinite discontinuous group of linear substitutions and the functions which are unchanged by it. This brilliant and fertile idea underlies the greater part of his work, and with its developments must be regarded as among the most valuable contributions to function-theory in recent years. In a series of masterly works, written partly alone and partly in collaboration with Prof. Fricke, he has extended this theory in detail, first for the case of algebraic functions, then for the modular functions, and finally for general automorphic functions.

No estimate of the debt that mathematical science owes to Prof. Klein would be satisfactory without some reference to his work as a teacher. He has created a school of young mathematicians at Göttingen whose work is a continuation of his own. His published lecture-courses on a variety of subjects are works of very great originality in method; and indeed, some of them—for instance, the course on the theory of numbers—abound in valuable original investigations.

The Rumford Medal.

This year the Rumford Medal has been awarded to Dr. Heike Kamerlingh Onnes, of Leyden, in recognition of the great value of his contributions to low-temperature research, among which his liquefaction of helium is the most noted. He has founded at Leyden the most thoroughly equipped laboratory in the world for investigations in low temperatures. In that institution a series of researches has been carried out regarding the effects of such great cold as can be obtained by the use of liquid hydrogen and even helium on the properties of substances, such as their magnetic relations and the electrical resistance of pure metals and alloys, the results of which are most striking and important for future progress. Prof. Onnes has also made valuable investigations on the nature of the transition between the solid and fluid states of matter.

The Royal Medals.

The awards of the two Royal Medals annually given by our Patron the King have received His Majesty's approval.

One of these medals has been assigned to our colleague, Prof. William Mitchinson Hicks, as a mark of the Society's appreciation of the value of his contributions to physical science. Among his researches may be specially mentioned those on hydrodynamics, and particularly on vortex motion, published in the 'Philosophical Transactions.' As a preparation for this work, he had previously made a very complete study and added much to our knowledge of a class of harmonic functions called by him "toroidal functions." He has also investigated, with a view to ultimate physical theories, the forces which exist between spheres immersed in an incompressible fluid medium when the volumes of the spheres are subject to periodical alterations. Of late years he has devoted much attention to the numerical relations which exist between the frequencies of lines belonging to the same spectral series, and has published expressions which give the relations between these frequencies with great accuracy. These investigations, which have involved much labour, have materially increased our knowledge of the spectra of groups of elements, and may probably prove of fundamental importance in relation to theories of the production of spectra in general.

The other Royal Medal has been adjudged to Prof. Grafton Elliot Smith, in recognition of the value of his biological investigations, more especially in regard to the morphology of the brain as developed in amphibians, reptiles, birds, monotremata, marsupials, and nearly every group of placental mammals. His researches have established the natural subdivisions of the cerebral hemispheres, and have shown that the development of the *neopallium*, in the co-ordination of sensory impulses, is the fundamental condition in the survival of mammals. His numerous papers are marked by a thorough grasp of the physiological and histological aspects of the subject and by great clearness of exposition.

Prof. Elliot Smith's work among the ancient cemeteries of Nubia may also be referred to. Already it has brought to light many interesting anatomical features in the buried remains of the former population of the Nile Valley, and, doubtless, much additional information will be obtained by him from the large mass of material which he has gathered together and brought to this country for deliberate study.

The Davy Medal.

The Davy Medal has been assigned to Prof. Otto Wallach for his researches in organic chemistry, particularly in regard to the essential oils. Our present knowledge of these complex vegetable products is largely the result of the numerous analytical investigations which he has carried out in the laboratories of Göttingen. He has made many important discoveries, more especially in connection with the cyclo-olefines and their derivatives, and his researches on these compounds have played a notable part in the general development of organic chemistry.

The Darwin Medal.

The Darwin Medal is this year awarded to one of the sons of the illustrious man in whose honour this Medal was founded twenty-two years ago. Mr. Francis Darwin by his researches has done much to emphasise the importance of plant movements in relation to environment, and has shown how strong is the evidence for the view that these various movements are the expression of the plant's own individuality in response to external stimuli, and that they have been developed or acquired by the plant as an adaptation to environment in the struggle for life. It is pleasant to remember that these interesting researches have been a continuation of the work which he carried on, conjointly with his father, in the long series of observations and experiments which are recorded in that important treatise, 'The Power of Movement in Plants.' Mr. Francis Darwin by his devotion to the Department of Vegetable Physiology at Cambridge has not only advanced botanical science by his own researches there, but through the stimulus of his enthusiasm has gathered round him a school of research which has attained a world-wide celebrity. To him, too, science is indebted for the admirable 'Life and Letters of Charles Darwin,' a work which by the vivid presentation of the life and character and work of one of the greatest naturalists the world has ever seen, by its modest self-effacement of the author, and by its literary charm, has unquestionably had a quickening influence on the advance of science in our time.

The Buchanan Medal.

This medal is awarded every five years in recognition of distinguished services to hygienic science or practice in the direction either of original research or of professional, administrative, or constructive work, without limit of nationality or sex. It has this year been adjudged to Colonel William Crawford Gorgas, for his remarkable services under the American Government, in combating the terrible scourge of yellow fever. As chief Sanitary Officer at Havana, Cuba, he there for the first time applied those sanitary methods by which the yellow fever was almost entirely eradicated from the place. This marked success led to his being entrusted in 1904 with a similar but greater task in the Panama Canal zone, where the same disease was rampant, and where he is still engaged. His success in that region has been not less conspicuous. Its attainment has required not only a complete knowledge of sanitary organisation in the Tropics, but also those administrative qualities which are necessary to ensure its practical enforcement. In the battle against diseases carried by insects, he led the way in the practical application of the results of scientific discovery, employing still untried weapons, and showing great fertility of resource and much needful determination in the face of many difficulties. He has earned the gratitude of mankind in having perfected a new method of saving human life on a large scale.

The Hughes Medal.

This medal has been adjudged to William Duddell, F.R.S., in recognition of the value of his researches in technical electricity and, in particular, his investigations with the oscillograph on telephonic sounds, his work on radio-telegraphy with the thermo-galvanometer, his development of the vibration galvanometer, and his investigations on the production of currents of very high frequency by the electric arc and by mechanical means.

The Motion of Viscous Liquid due to Uniform and Periodic Motion Maintained over a Segment of an Infinite Plane Boundary.

By W. J. HARRISON, M.A., Fellow of Clare College, Cambridge; Assistant Lecturer in Mathematics, University of Liverpool.

(Communicated by Sir J. Larmor, Sec. R.S. Received October 14,—Read November 21, 1912.)

The author was led to a consideration of the problems whose solutions are presented in this paper by the attempt to solve a certain problem in the theory of lubrication. But it was thought that these solutions have sufficient intrinsic interest to warrant their separate publication as examples in theoretical hydrodynamics, the more physical applications to lubrication being reserved for further development.

In the first three problems infinite viscous liquid is maintained in motion by uniform or periodic tangential motion of a part (a strip of infinite length) of its plane boundary. In the remaining two problems the liquid is further limited by a second plane boundary parallel to the first.

A departure, which may be more or less important, from the usual actual physical conditions is necessitated by the result that it is impossible to maintain the condition of no relative velocity at the boundary. The treatment of the problem with the condition of no slip leads to a discontinuity in the velocity of the liquid at the boundaries of the moving strip. But, on the other hand, from the nature of the problem this condition of no slip is an impossible physical state of affairs in the neighbourhood of two lines of the boundary. This complexity is avoided if we take the more general condition of slip with tangential traction proportional to the relative velocity, and then the case of no slip will be approached by taking the ratio of traction to slip to increase indefinitely. There are two other alternative suppositions which might be made and which seem to carry with them a more physical appearance. These will have to be examined before further applications are made of these solutions, but the solutions in their present form are given for their own interest.

Problem 1.

In this and the following calculations the motion is two-dimensional, and will therefore be considered to take place in the x, y plane; accordingly, the third co-ordinate will never be mentioned.

Viscous liquid occupies the part of the x, y plane for which y is positive, being bounded by the axis of x. This boundary is fixed, except that between $x = \pm\xi$ it is given a uniform velocity ϖ in its own direction. The effect may be produced by supposing the part of the axis $-\xi < x < \xi$ cut away, and underneath in contact with it a second boundary is placed which moves with the given velocity. It is required to determine the motion which is thus maintained.

The motion is steady and is, moreover, assumed to be slow.* It follows that the stream function satisfies the equation $\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)^2\psi = 0$.

If we assume a disturbance depending on $\cos kx$, then

$$\psi = (Ae^{-ky}+Bye^{-ky})\cos kx,$$

where k is positive. This form of the stream function is appropriate to a velocity along the bounding plane varying as $\cos kx$. Let the velocity of the boundary in its own direction be $\varpi_k \cos kx$.

It is impossible to satisfy the condition of no relative motion at the boundary owing to the discontinuity that would arise at the points $x = \pm\xi$, $y = 0$ in the final synthesis of the harmonic elements. Accordingly, the assumption is made that the boundary exerts a traction on the liquid proportional to the relative velocity. Thus

$$\frac{\partial\psi}{\partial y}-\lambda\frac{\partial^2\psi}{\partial y^2} = \varpi_k \cos kx \quad (y = 0),$$

is the appropriate condition. If λ be made very small the condition of no relative velocity is approximately satisfied in general.

The remaining boundary condition is $\psi = 0 \quad (y = 0)$.

These lead to

$$A = 0, \qquad B = \varpi_k/(1+2\lambda k).$$

If the distribution of velocity of the boundary in its own direction be given by $f(x)$, then

$$\psi = \frac{1}{\pi}\int_0^\infty dk\int_{-\infty}^\infty \frac{f(\alpha)}{1+2\lambda k}\,ye^{-ky}\cos k(x-\alpha)\,d\alpha.$$

Suppose
$$f(\alpha) = \varpi, \qquad -\xi < x < \xi,$$
$$f(\alpha) = 0, \qquad x < -\xi, \qquad x > \xi.$$

* The fact that the motion has to be assumed slow in order to obtain linear equations is a very serious limitation on the interest of the solution; but it must be noticed that when it is a question of motion between parallel planes which are very near together the non-linear terms are neglected by Osborne Reynolds in his paper on lubrication, for physical reasons, and the limitation of slow motion is thus removed. This consideration applies to the last two problems.

Hence

$$\psi = y\frac{\varpi}{\pi}\int_0^\infty \frac{e^{-ky}}{k(1+2\lambda k)}[\sin k(\xi+x)+\sin k(\xi-x)]\,dk$$

$$= y\frac{\varpi}{\pi}\left\{\tan^{-1}\frac{\xi+x}{y}+\tan^{-1}\frac{\xi-x}{y} - \int_0^\infty \frac{2\lambda e^{-ky}}{1+2\lambda k}[\sin k(\xi+x)+\sin k(\xi-x)]\,dk\right\}.$$

A convenient method of evaluating the definite integral is to plot the integrand for particular numerical values of x, y, ξ, λ. But it is to be noticed that if λ be small, say $\lambda = 0{\cdot}01$, then, except near the boundary, ψ is given by the integrated terms to a high degree of approximation.

In fig. 1 the stream lines are shown for the case $\lambda = 0{\cdot}01$, $\xi = 1$. They are drawn for the equidistant values $(\frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{5}{3})\,\varpi/\pi$ of the stream function. They are, however, independent of λ.

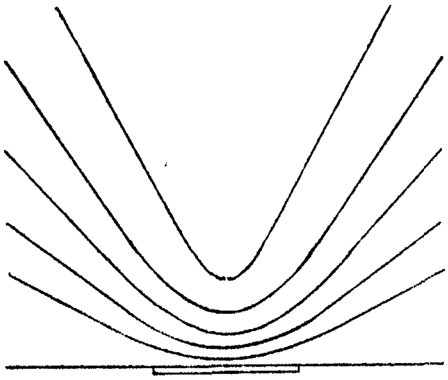

Fig. 1.

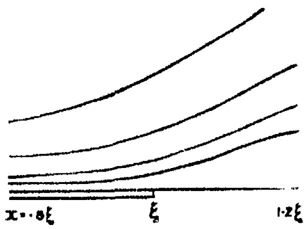

Fig. 2.

In fig. 2 the stream lines are drawn in the neighbourhood of $x = 1$, $y = 0$ for the same case. The method of evaluating the integral is similar to one to be mentioned later. The stream lines are drawn for

$$\psi = (0{\cdot}03,\ 0{\cdot}06,\ 0{\cdot}12,\ 0{\cdot}24)\,\varpi/\pi.$$

Distribution of Velocity along the Axis of x.

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0} = \frac{\varpi}{\pi}\int_0^\infty \frac{\sin k(\xi+x)+\sin k(\xi-x)}{k(1+2\lambda k)}\,dk.$$

Now $$\int_0^\infty \frac{\sin ak}{b+k}\,dk = \int_{ab}^\infty \frac{\sin(m-ab)}{m}\,dm \quad (\text{provided } a>0)$$

$$= \left(\frac{\pi}{2}-\mathrm{Si}\,(ab)\right)\cos(ab)+\mathrm{Ci}\,(ab)\sin(ab).$$

Hence

$$\left(\frac{\partial \psi}{\partial y}\right)_{y=0} = \varpi - \frac{\varpi}{\pi}\left[\left(\frac{\pi}{2} - \mathrm{Si}\,\theta\right)\cos\theta + \mathrm{Ci}\,\theta\sin\theta + \left(\frac{\pi}{2} - \mathrm{Si}\,\phi\right)\cos\phi + \mathrm{Ci}\,\phi\sin\phi\right], \quad 0 < x < \xi,$$

$$= -\frac{\varpi}{\pi}\left[\left(\frac{\pi}{2} - \mathrm{Si}\,\theta\right)\cos\theta + \mathrm{Ci}\,\theta\sin\theta - \left(\frac{\pi}{2} - \mathrm{Si}\,\phi\right)\cos\phi - \mathrm{Ci}\,\phi\sin\phi\right], \quad x > \xi,$$

where $\theta = (\xi + x)/2\lambda, \qquad \phi = |\xi - x|/2\lambda.$

The distribution of the velocity along the boundary, of which the moving section is bounded by $x = \pm 1$, is exhibited in the following table. The evaluation has been performed by the aid of Glaisher's Tables of the Sine and Cosine Integrals.

λ.	$x = 0$.	0·6.	1.	1·4.	2.	3.
0·01	0·987	0·98	0·497	0·013		
0·1	0·88	0·833	0·469	0·101	0·030	
1	0·452	0·416	0·303	0·183	0·119	0·017

The table shows the ratio of the velocity to ϖ.

In addition to the above values it is interesting to note, in the case of $\lambda = 0{\cdot}01$, how rapidly the velocity changes in the neighbourhood of $x = 1$.

$$x = 0{\cdot}9 \;\ldots\ldots\ldots\; u = 0{\cdot}937\,\varpi,$$
$$x = 0{\cdot}99 \;\ldots\ldots\ldots\; u = 0{\cdot}713\,\varpi,$$
$$x = 1 \;\ldots\ldots\ldots\; u = 0{\cdot}497\,\varpi.$$

From the distribution of the relative velocity of the sliding piece and the liquid in contact with it, the traction ($\mu\,\partial^2\psi/\partial y^2$, $y = 0$) exerted by the one on the other can be directly obtained,

$$\mu\frac{\partial^2\psi}{\partial y^2} = -\frac{\mu}{\lambda}\left(\varpi - \frac{\partial\psi}{\partial y}\right), \qquad y = 0,$$

where μ is the coefficient of viscosity.

The total traction exerted by the liquid on the sliding piece per unit of its length is given as follows:—For the values 0·01, 0·1, 1 of λ, traction/$\mu\varpi$ has the values 3·1, 1·6, 0·56, the breadth being two units.

The total rate of flow in the direction of motion of the sliding piece is $2\varpi\xi/\pi$, and this is independent of λ. This is to be explained by the fact that, although the sliding piece exerts less traction on the liquid the greater the value of λ, the liquid itself experiences less resistance from the remainder of the boundary.

Problem 2.

From the foregoing solution it is possible to derive immediately the stream lines where there are two such sliding pieces in different parts of the boundary.

In fig. 3 the stream lines are drawn for the case when the part of the boundary $1 < x < 3$ is given a velocity ϖ in the direction of x, and the part $-1 > x > -3$ is given an equal velocity in the opposite direction. The stream lines are drawn for the equidistant values $(0{\cdot}5, 0{\cdot}75, 1, 1{\cdot}25, 1{\cdot}5)\, \varpi/\pi$ of the stream function.

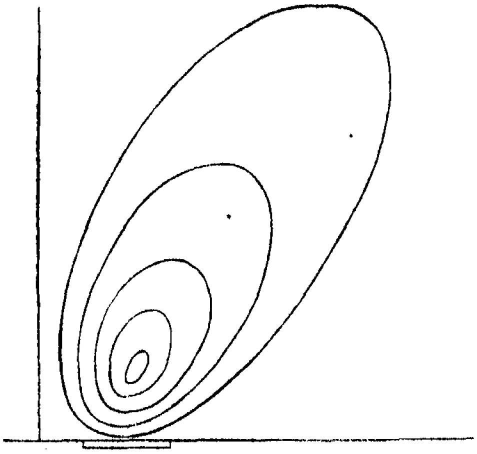

FIG. 3.

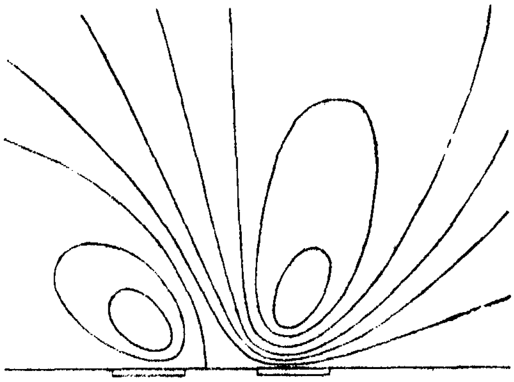

FIG. 4.

In fig. 4 the stream lines are drawn for the case in which the velocity of the second sliding piece is half that of the first. The lines are shown for the same values of ψ as in the previous case, except that $\psi = 0{\cdot}25\, \varpi/\pi$ is drawn as well.

Problem 3.

We proceed to consider the case in which the sliding piece, instead of having a uniform velocity, is given a periodic velocity $\varpi \cos pt$.

The stream function must now satisfy the equation

$$\left(\nu\nabla^2 - \frac{\partial}{\partial t}\right)\nabla^2\psi = 0,$$

where ν is the kinematic coefficient of viscosity.

The appropriate solution is

$$\psi = (\mathrm{A}e^{-ky} + \mathrm{B}e^{-my}) \cos kx e^{ipt}, \quad \text{where} \quad m^2 = k^2 + ip/\nu,$$

leading to
$$m = q + i\mu,$$

q being taken positive. Also, since we are concerned with a maintained motion, p is real.

The axis of x is a stream line, and therefore

$$A+B = 0.$$

This solution is appropriate to the harmonic distribution of velocity $\varpi_k \cos kx\, e^{ipt}$ of the boundary. Hence the remaining boundary condition is

$$\frac{\partial\psi}{\partial y}-\lambda\frac{\partial^2\psi}{\partial y^2} = \varpi_k \cos kx\, e^{ipt} \qquad (y = 0).$$

This leads to $\qquad -(k+\lambda k^2)\,A-(m+\lambda m^2)\,B = \varpi_k.$

Hence $\qquad A = -B = \varpi_k/(m-k+i\lambda p/\nu).$

Taking real parts, we find

$$\psi = \varpi_k F(k) \cos kx,$$

where

$$F(k) = [e^{-ky}(P\sin pt+Q\cos pt)-e^{-qy}\{P(\cos\mu y\sin pt-\sin\mu y\cos pt) + Q(\cos\mu y\cos pt+\sin\mu y\sin pt)\}]/(P^2+Q^2),$$

where $\qquad P = \mu+\lambda p/\nu, \qquad Q = q-k.$

The solution, following the notation of Problem 1, is

$$\psi = \frac{\varpi}{\pi}\int_0^\infty [\sin k(\xi+x)+\sin k(\xi-x)]\frac{F(k)}{k}\,dk.$$

The work of calculating the stream lines for particular values of the constants involved is a matter of some complexity. I have performed it for one case, but not sufficiently to give more than a rough idea of their form. But it was possible to see that a vortex is periodically formed and destroyed in the neighbourhood of the sliding piece in this particular case. It would be interesting to trace the stream lines for a range of values of the time, and so exhibit the growth and decay of this vortex. But at the present time I have not the requisite leisure.

Distribution of Velocity over the Sliding Piece.—It can easily be shown that

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0} = \frac{\varpi}{\pi}\int_0^\infty [\sin k(\xi+x)+\sin k(\xi-x)]\times\left[\left(1-\frac{P\lambda p/\nu}{P^2+Q^2}\right)\cos pt + \frac{Q\lambda p/\nu}{P^2+Q^2}\sin pt\right]\frac{dk}{k}.$$

The numerical evaluation of this integral presents features of some interest. Apart from x the variables are ξ, λ, p/ν; ξ has been taken equal to one unit as before, $\lambda = 0{\cdot}01$, and the integral has been evaluated for

$$p/\nu = 10^{-1},\ 1,\ 10,\ 10^2,\ 10^3,\ 10^4,\ 10^6.$$

The method of evaluation depends upon the magnitude of p/ν, and one or two illustrations of the methods employed will be given.

(*a*). $p/\nu = 0{\cdot}1$.

$$\int_0^\infty \frac{\mathrm{P}}{\mathrm{P}^2+\mathrm{Q}^2}\sin k(\xi+x)\frac{dk}{k} = \int_0^2 \frac{\mathrm{P}}{\mathrm{P}^2+\mathrm{Q}^2}\sin k(\xi+x)\frac{dk}{k} + \int_2^\infty \frac{\sin k(\xi+x)}{\mathrm{P}}\frac{dk}{k},$$

since Q is very small for $k > 2$. At the same time $\mu = p/2k\nu$, so that the second integral is capable of evaluation by the aid of the tables of sine and cosine integrals as in similar integrals in Problem 1. The first integral can be evaluated by plotting the integrand.

In this same case the coefficient of $\sin pt$ can be evaluated by plotting the integrand, since it decreases rapidly with k.

(*b*). $p/\nu = 10$.

The coefficient of $\varpi \cos pt$ (for $x = 0$) involves an integral which can be replaced by

$$\int_0^6 (0{\cdot}223 + 0{\cdot}105\,k + 0{\cdot}0063\,k^2)\frac{\sin k}{10k}\,dk + \int_6^\infty \frac{\sin k\,dk}{50+k}$$

to a good degree of accuracy. These integrals are easily evaluated.

(*c*). $p/\nu = 10^4$.

The coefficient of $\varpi \cos pt$ (for $x = 0$) involves an integral which can be replaced by

$$\int_0^{100} (0{\cdot}005 + 0{\cdot}0000184\,k)\frac{\sin k}{k}\,dk.$$

Or (*d*). $p/\nu \geq 10^4$.

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0} = \varpi\left[\left(1 - \frac{\mathrm{P}\lambda p/\nu}{\mathrm{P}^2+\mathrm{Q}^2}\right)\cos pt + \frac{\mathrm{Q}\lambda p/\nu}{\mathrm{P}^2+\mathrm{Q}^2}\sin pt\right],$$

for any value of x between $\pm\xi$, except near these limits.

When p/ν is very great $\left(\dfrac{\partial\psi}{\partial y}\right)_{y=0} = 0$.

Representing the velocity at the centre of the sliding piece by $\mathrm{X}\cos pt + \mathrm{Y}\sin pt$, we have the following values for X and Y.

p/ν	10^{-1}.	1.	10.	10^2.	10^3.	10^4.	10^6.
X	0·99	0·99	0·97	0·98	0·79	0·5	0·07
Y	0·001	0·005	0·025	0·06	0·15	0·21	0·06

X decreases from 1 to 0, Y increases from 0 to a maximum value and then decreases again to zero. The velocity at the point $x = \frac{1}{2}\xi$ is 1 or 2 per cent.

C 2

below that at the centre, and at $x = \xi$, X and Y have practically half their values at the centre.

The maximum (as regards the time) integral traction on the sliding piece per unit of its length can easily be found. It has the following values in units of the system of measurements employed.

p/ν	10^{-1}.	1.	10.	10^2.	10^3.	10^4.	10^5.
Traction $\mu\varpi$	3	3	14	23	55	114	190

For water, $p/\nu = 10^3$ corresponds to a period of 0·6 sec. in C.G.S. units, so that for this period the traction is about 18 times that for steady motion.

Problem 4.

This is the same as the first problem, except that the liquid is further bounded by $y = b$, which is fixed. The corresponding boundary condition is taken to be that no relative motion is possible over it.

A possible stream function is given by

$$\psi = \{(A+Cy)\sinh ky + (B+Dy)\cosh ky\} \cos kx.$$

The conditions to be satisfied are

$$\psi = 0, \qquad \frac{\partial\psi}{\partial y} - \lambda\frac{\partial^2\psi}{\partial y^2} = \varpi_k \cos kx \qquad (y = 0);$$

$$\psi = 0, \qquad \frac{\partial\psi}{\partial y} = 0 \quad (y = b).$$

These lead to $B = 0$, and

$$\frac{A}{-kb^2} = \frac{C}{kb - \frac{1}{2}\sinh 2kb} = \frac{D}{\sinh^2 kb}$$

$$= \frac{\varpi_k}{-k^2b^2 - 2k^2b\lambda + k\lambda\sinh 2kb + \sinh^2 kb} = \frac{\varpi_k}{\phi(k)}.$$

Using Fourier's theorem, we obtain the stream function in the form

$$\psi = \frac{\varpi}{\pi}\int_0^\infty [\sin k(\xi + x) + \sin k(\xi - x)]\frac{\chi(k)}{\phi(k)}\frac{dk}{k},$$

where

$$\chi(k) = [-kb^2 + (kb - \tfrac{1}{2}\sinh 2kb)\,y]\sinh ky + y\sinh^2 kb\cosh ky.$$

In fig. 5 the stream lines are drawn for the case of $\xi = 1$, $b = 2$, $\lambda = 1$. Since calculating ψ for the unpractical case of $\lambda = 1$, I have lighted upon a method of evaluating the integral for $\lambda = 0{\cdot}01$, but the advantage of recalculation is not great in the case of b so great as 2.

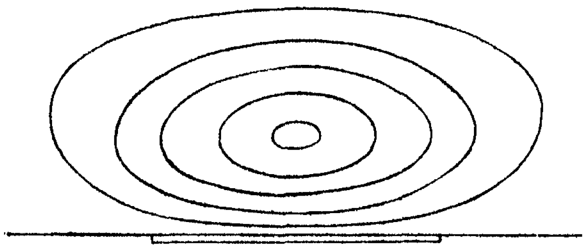

FIG. 5.

Velocity of the Liquid at the Centre of the Sliding Piece.—The expression for the velocity of the liquid along the boundary $y = 0$ is

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0} = \frac{\varpi}{\pi}\int_0^\infty \frac{-k^2b^2+\sinh^2 kb}{k\phi(k)}[\sin k(\xi+x)+\sin k(\xi-x)]\,dk.$$

The ratio of the velocity at the centre of the sliding piece to ϖ is given below :—

λ.	$b = 1$.	0·1.	0·01.
0·01	0·96	0·72	0·2
0·1	0·71	0·2	0·025

When b is small, it is easily shown that the velocity at any point of the sliding piece is $b\varpi/(b+4\lambda)$, except that the approximation breaks down when $\xi-x$ is small, and that at $x = \xi$ the velocity drops to half that at the centre.

Hence the traction exerted by the liquid on the sliding piece is (per unit length)

$$\frac{2\varpi\xi}{\lambda}\left(1-\frac{b}{b+4\lambda}\right)\mu = \frac{8\mu\varpi\xi}{b+4\lambda}.$$

As b is decreased indefinitely, this approaches the limit $2\mu\varpi\xi/\lambda$. This is the same limit as in the case of the rapid periodic motion of the last case.

Problem 5.

The liquid is bounded by two parallel planes as in the previous case, but the sliding piece is given a periodic velocity $\varpi\cos pt$.

The appropriate typical harmonic solution is

$$\psi = (\mathrm{A}\cosh ky+\mathrm{B}\sinh ky+\mathrm{C}\cosh my+\mathrm{D}\sinh my)\cosh kx\, e^{ipt},$$

with the same notation as in Problem 3.

The solution follows as in previous cases, and I proceed at once to discuss the velocity of the liquid at points on the sliding piece.

Consider $\int_0^\infty \frac{\sin k}{k} f(k)\, dk.$

If $f(k)$ vary slowly with k within the range $0 < k < 20$ (say), the value of the integral is $\frac{1}{2}\pi f(0)$ to a very fair degree of accuracy.

It is assumed that $f(k)$ is decreasing and one-signed. The rate of variation need not be very slow for the approximation to hold, for example $f(k)$ may decrease practically to zero in the interval. The approximations which follow are based on this consideration, but it is not claimed that the intermediate results in the range are more than roughly correct.

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0} = \frac{\varpi}{\pi}\int_0^\infty [\sin k(\xi+x)+\sin k(\xi-x)]\frac{f(k)}{k}\, dk,$$

where $f(k)$ is the real part of e^{ipt} divided by

$$1+\frac{i\lambda p}{\nu}\cdot\frac{m\sinh kb\cosh mb - k\cosh kb\sinh mb}{2km(1-\cosh kb\cosh mb)+(k^2+m^2)\sinh kb\sinh mb}.$$

Now, provided b be small, the variation in $f(k)$ is small for moderate values of k. Accordingly $f(k)$ is replaced by $f(0)$.

Now, when $k=0$, $m = q+i\mu$, where $q=\mu=(p/2\nu)^{\frac{1}{2}} = \alpha$ (say).

Put $\alpha b = \eta$, $\lambda\alpha = \zeta$.

It is found that

$$\left(\frac{\partial\psi}{\partial y}\right)_{y=0,\, x=0} = \varpi(\mathrm{R}\cos pt+\mathrm{S}\sin pt)/\mathrm{T},$$

where

$$\begin{aligned}\mathrm{R} = {} & 2-4\cosh\eta\cos\eta-2\eta\zeta\sinh\eta\sin\eta+\cosh 2\eta+\cos 2\eta \\ & -(2\eta-\zeta)(\cosh\eta\sin\eta-\sinh\eta\cos\eta)+\tfrac{1}{2}(2\eta-\zeta+\eta^2\zeta)\sin 2\eta \\ & -\tfrac{1}{2}(2\eta-\zeta-\eta^2\zeta)\sinh 2\eta+\tfrac{1}{2}\eta(\eta-\zeta)(\cosh 2\eta-\cos 2\eta),\end{aligned}$$

$$\begin{aligned}\mathrm{S} = {} & \zeta[\eta(\cosh 2\eta+\cos 2\eta-2\cosh\eta\cos\eta)-\tfrac{1}{2}(1+\eta^2)\sinh 2\eta \\ & -\tfrac{1}{2}(1-\eta^2)\sin 2\eta+(\cosh\eta\sin\eta+\sinh\eta\cos\eta)],\end{aligned}$$

$$\begin{aligned}\mathrm{T} = {} & 2-4\cosh\eta\cos\eta-4\eta\zeta\sinh\eta\sin\eta-2(\eta-\zeta)(\cosh\eta\sin\eta \\ & -\sinh\eta\cos\eta)+(\eta-\zeta)(1+\eta\zeta)\sin 2\eta-(\eta-\zeta)(1-\eta\zeta)\sinh 2\eta \\ & +(1+\eta^2\zeta^2)(\cosh 2\eta+\cos 2\eta)+\tfrac{1}{2}(\eta-\zeta)^2(\cosh 2\eta-\cos 2\eta).\end{aligned}$$

(*a*) Approximation when αb is small.—

The velocity at the centre of the sliding piece is equal to $\frac{b}{b+4\lambda}\varpi\cos pt$, the coefficient being the same as in the case of steady motion.

This approximation is valid if (1) $b = 0{\cdot}1$ cm., $\alpha \leq 1$, which gives for water a period of 5 mins. and over, (2) $b = 0{\cdot}01$ cm., $\alpha \leq 10$, which gives for water a period of 3 sec. and over.

(*b*) Approximation when $\alpha b \geqq 4$, so that $\cosh \alpha b$ and $\sinh \alpha b$ can be neglected, compared with $\cosh^2 \alpha b$, etc.—

This applies in the case of water to periods of 0·2 second and under, and 0·002 second and under, for the cases $b = 0·1$ and $b = 0·01$ respectively.

The velocity at the centre of the sliding piece is

$$\varpi\,[\{1-\tfrac{1}{2}(2\eta-\zeta-\eta^2\zeta)+\tfrac{1}{2}\eta(\eta-\zeta)\}\cos pt$$
$$+\{\eta\zeta-\tfrac{1}{2}\zeta(1+\eta^2)\}\sin pt]/[(1+\eta^2\zeta^2)+\tfrac{1}{2}(\eta-\zeta)^2-(\eta-\zeta)(1-\eta\zeta)].$$

The following table includes the whole range of values of αb, for $\lambda = 0·01$ $b = 0·01$, in which case $\eta = \zeta$, and the above formula is simplified.

αb......	0·01.	0·1.	1.	2.	3.	4.	5.	6.	10.
R/T......	0·2	0·2	0·199	0·19	0·157	0·121	0·097	0·083	0·05
−S/T......	0	0	0·011	0·088	0·082	0·07	0·064	0·056	0·05

It follows that the traction exerted on the sliding piece bears a ratio to that exerted in the steady motion which lies between 1 and $(b + 4\lambda)/4\lambda$.

It will be noticed in Problem 3 when the period of the motion is very small, and in both of the last two problems when b is small, that the condition of no slip at the boundary is not approximately satisfied for $\lambda = 0·01$. If λ be taken sufficiently small, then it is easily shown that the maximum total traction per unit length on the moving piece has a value $2\mu\varpi\xi(p/\nu)^{\frac{1}{2}}$, in the case of very rapid motion in Problem 3. In the steady motion of Problem 4, when the distance b between the two planes is very small, the integral traction has the value $8\mu\varpi\xi/b$. In the periodic motion of Problem 5, if b be small and $b\,(p/2\nu)^{\frac{1}{2}} < 0·1$, the integral traction depends upon b and not upon p, and has the maximum value $8\mu\varpi\zeta/b$. If, however, b be small and p sufficiently great, the traction is independent of b and has the value $2\mu\varpi\xi(p/\nu)^{\frac{1}{2}}$. This can be shown from the approximate expressions for R/T, S/T, which are given above.

Thus in the case of periodic motion between two near parallel planes the integral traction is equal to or greater than $8\mu\varpi\xi/b$, and less than or equal to $2\mu\varpi\xi(p/\nu)^{\frac{1}{2}}$, provided this second limit is greater than the first.

A Comparison of the Spectra of Fluorescent Röntgen Radiations.

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(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received October 22,—Read November 21, 1912.)

In a previous paper* published in the 'Proceedings of the Royal Society,' it has been shown that there is a second group of elements consisting of tungsten, gold, platinum, bismuth, and the radioactive elements uranium and thorium, which emit secondary fluorescent X-radiation when excited by a suitable primary beam of Röntgen rays. The properties which the radiations of this group (Group L) have been shown to possess in common with the radiations of Group K (elements Cr–I), investigated some years ago by Prof. Barkla,† are as follows:—(1) The radiations emitted by any particular element when excited consist of two distinct types: (*a*) the scattered radiation, having the same penetrating power as the primary beam and indistinguishable from it; (*b*) the homogeneous X-radiation characteristic of the particular element in question. (2) Each element exerts a selective absorption for radiations which are of such a degree of hardness that they lie in the neighbourhood of an "absorption band."

In the case of the elements of Group L, to demonstrate the homogeneity of the radiations, allowance had to be made for the scattered radiation which always accompanies the homogeneous constituent, but which in the case of the heavier elements is present in such magnitude as to mask, if no correction is applied, the true homogeneity. In the experiment described in the paper referred to, the absorption in aluminium of the various radiations has been measured. In Tables I and II the absorption coefficient (λ/ρ) is defined by the equation $I = I_0 e^{-\lambda x}$, where ρ is the density of aluminium.

The absorption coefficients in aluminium of the radiations of Group K are added for reference (Table II).

From these tables it will be seen that the penetrating power of the radiations in Group L is of the same order as the penetrating power of the radiations in Group K. The following empirical equation connects the atomic weights of two elements, which, though in different groups, emit characteristic

* Chapman, 'Roy. Soc. Proc.,' 1912, A, vol. 86.

† Barkla and Sadler, 'Phil. Mag.,' October, 1908.

Table I.

Element in Group L emitting radiation.	Atomic weight of element.	λ/ρ in Al of radiation.
Tungsten	184 ·0	30 ·0
Platinum	195 ·0	22 ·2
Gold	197 ·2	21 ·6
Lead	207 ·0	17 ·4
Bismuth	208 ·5	16 ·1
Thorium	232 ·0	8 ·0
Uranium	238 ·0	7 ·5

Table II.

Element in Group K emitting radiation.	Atomic weight of element.	λ/ρ in Al of radiation.
Copper	63 ·6	47 ·7
Zinc	65 ·4	39 ·4
Arsenic	75 ·0	22 ·5
Selenium	79 ·2	18 ·9
Bromine	80 ·0	16 ·3
Strontium	87 ·6	9 ·4
Molybdenum	96 ·0	4 ·7
Silver	107 ·9	2 ·5

radiations which appear the same when measured simply by their absorption in aluminium :—

$$W_K = \tfrac{1}{2}(W_L - 48).$$

The results then up to the present can be stated as follows :—Two elements of different atomic weights and belonging to different groups as regards their periodic X-ray significance can, if suitably excited by a primary beam of Röntgen rays, be caused to emit identical characteristic radiations, when the sole criterion of identity is the fact that the absorption coefficients of their radiations in aluminium are equal.

This second series (Group L) is of great importance from the point of view of X-ray properties, but the results given in the previous paper cannot, without further experiment, be employed with any certainty for the purpose of throwing light on the internal structure of matter, which is one of the objects of detailed X-ray study. The results cannot be directly used, for this reason : the comparison of the radiations of both groups, and the only way in which both have been standardised, is by means of their property of being absorbed to different extents in aluminium. Now this test by itself is far from sufficient ; the absorption in a single element—in fact, absorption experiments alone—cannot determine conclusively the X-ray property of an element, for two radiations totally different in structure might conceivably

be absorbed to the same extent in the one element aluminium. In addition to this, even if equal absorptions take place, there is yet the possibility that the energy absorbed is not transformed in similar ways for the two radiations.

It is the object of the present paper to investigate in some detail the radiations of the two groups, so as to establish the identity or dissimilarity of the types of radiation. If we imagine for a moment that two totally different types of radiation can be produced in any way, yet having equal absorption coefficients in an element X, then, tested only by their absorption in X, they would appear identical. Suppose now instead of measuring their absorption in X their absorption in another element Y be found. If the two radiations are not identical or of very similar nature, there is no reason for supposing that their absorption coefficients in the new element Y would again be identical.

This method of investigating the radiations of the two groups was the first used in the experiment. The absorption in aluminium of the radiations of Group K and Group L being known, the absorption of the radiations of both groups was measured in various elements other than aluminium, in order to see whether the absorptions of two radiations in different groups, having the same absorption coefficients in aluminium, were also equal in these other elements.

Absorption Experiments.

The apparatus was essentially similar to that used in the previous research.

The usual method of exhibiting the absorption of the spectrum of homogeneous radiations by any element is as follows:—The absorption coefficients (λ/ρ) in the element X of the various radiations are plotted as ordinates, while the absorption coefficients (λ/ρ) in aluminium for the same radiations are plotted as abscissæ. In this way a curve is obtained showing the relation between the absorption coefficients in the element X and in aluminium. Since there are two groups of elements furnishing X-ray spectra, this curve can be obtained in two different ways. Suppose we consider that this curve has been plotted, using the elements of Group K as the series of radiations absorbed, that is λ/ρ in X has been plotted against λ/ρ in aluminium (Group K). Now consider that another curve is drawn, but in this case the group of elements which furnish the series or spectrum of radiations must be Group L. When this is done we again have λ/ρ in X plotted against λ/ρ in aluminium (Group L), the only difference being that in the latter case the various radiations having different values of λ/ρ in aluminium belong to the second Group L and not to Group K as in the first curve. The point in question is whether the form of curve is the same in the two cases.

In order to test this, the following absorptions were successively determined. The absorption by copper, silver, and platinum, of—

(1) The characteristic radiations of Group K.

(2) The characteristic radiations of Group L.

Each of these three elements was selected because of its definite X-ray significance. The element copper belongs to Group K, and its homogeneous characteristic radiation is excited by the whole series of radiations (Group L), the absorption of which was determined. Silver also belongs to Group K, but its characteristic radiation is not excited by any element in Group L. The element platinum belongs to Group L, and, in addition, platinum exerts a selective absorption for a range of radiations which falls in the spectra formed by both Group K and Group L.

In the case of the absorption of the radiations of Group K, it is only necessary to determine those of bromine, strontium, and molybdenum radiations. The other values have been previously found.* As before, λ/ρ is defined by the equation $I = I_0 e^{-\lambda x}$, while ρ is the density of the element absorbing.

ABSORPTION TABLES.

Table III.—For Radiations of Group K.

Element emitting radiation.	λ/ρ in Al of radiation.	λ/ρ in Cu of radiation.	λ/ρ in Ag of radiation.	λ/ρ in Pt of radiation.
Br	16·3	128·5	75·4	180·7
Sr..................	9·4	83·4	48·8	180·0
Mo	4·8	40·3	24·4	95·5

Table IV.—For Radiations of Group L.

Element emitting radiation.	λ/ρ in Al of radiation.	λ/ρ in Cu of radiation.	λ/ρ in Ag of radiation.	λ/ρ in Pt of radiation.
W	30·0	127·1	140·3	132·7
Pt	22·2	177·0	106·4	113·0
Pb	17·4	139·1	77·5	128·5
Bi	16·1	126·7	72·9	125·0
Th	8·0	76·6	42·3	138·7
Ur	7·5	70·2	40·3	132·0

From results previously obtained, combined with the two tables just given, it is possible to show that, for the various radiations of Group L, the ratio of λ/ρ in Cu of any radiation in Group L to λ/ρ in Cu of radiation in

* Barkla and Sadler, 'Phil. Mag.,' May, 1909.

Group K having same λ/ρ in Al as radiation of Group L is unity. This ratio B/A is found in the fifth column of Table V. It is also given in Table VI for the silver and platinum absorptions.

Table V.

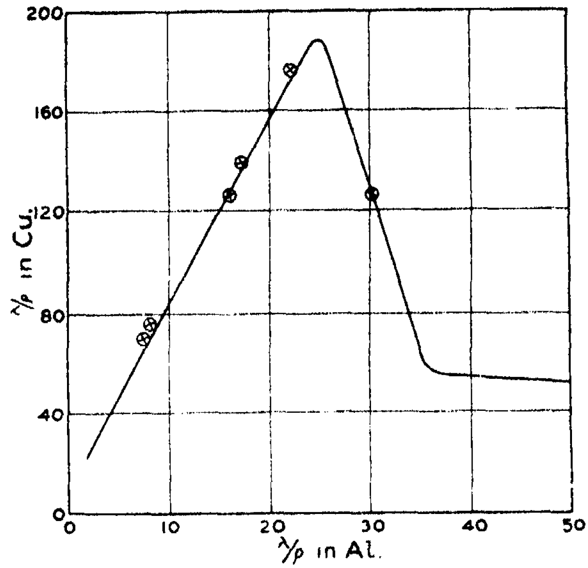
Element emitting radiation.	λ/ρ in Al of radiation.	λ/ρ in Cu of radiation. A.	λ/ρ in Cu of radiation of Group K having same λ/ρ in Al as radiation of Group L. B.	Ratio B/A.
W	30·0	127·1	128	1·0
Pt	22·2	177·0	174	0·99
Pb	17·4	139·1	138	0·99
Bi	16·1	126·7	127	1·0
Th	8·0	76·6	70	0·92
Ur	7·5	70·2	66	0·94

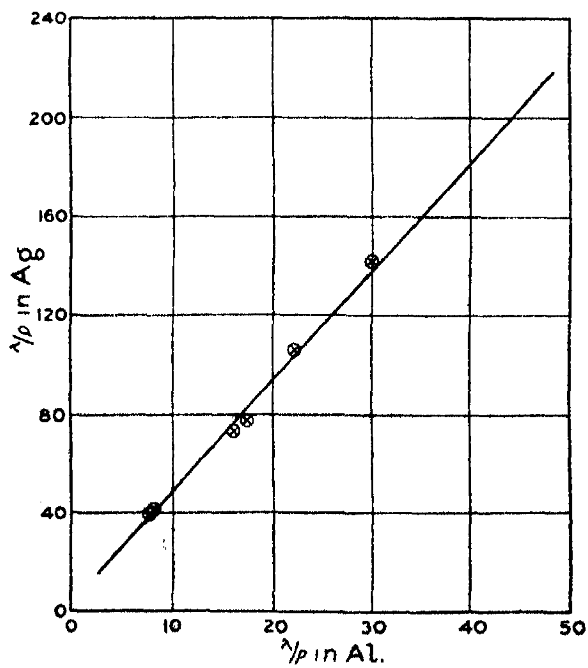
Table VI.

Element emitting radiation.	Ratio B/A silver absorbing.	Ratio B/A platinum absorbing.
W	0·99	1·0
Pt	0·97	0·94
Pb	1·05	1·0
Bi	1·04	1·5*
Th	1·0	1·09
Ur	0·97	1·04

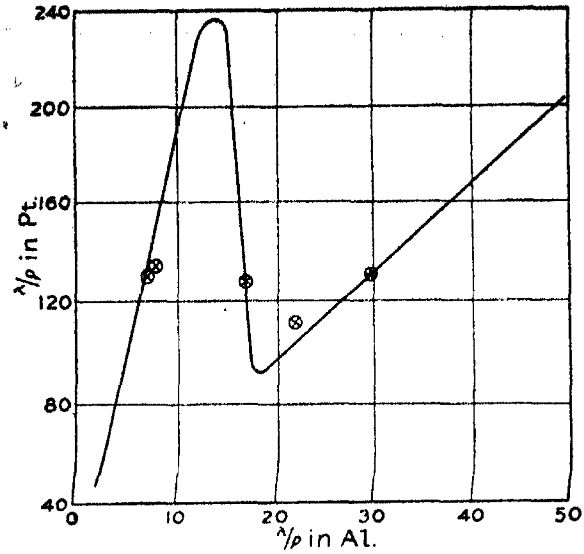
* The curve showing the relation between λ/ρ in Pt and λ/ρ in Al is so steep at this point that a small inaccuracy in observation would introduce this discrepancy.

The fact that the ratio in each of the three cases approximates to unity can be exhibited graphically by drawing the curves for copper, silver, and platinum respectively, showing the relation between the absorption in the particular element and the absorption in aluminium for the spectra of radiations formed by each group. In the curves, the continuous lines indicate the absorption of the radiations of Group K. It will be seen that the points corresponding to the radiations of Group L lie approximately on the same curve. This fact, that a single curve results on which lie the values of the absorption coefficients for both series of radiations (Group K and Group L), proves that the radiations in the two groups are of a similar nature. Had the radiations been dissimilar, and had it only been by accident that the absorption coefficients in aluminium bear a certain relation to one another, two curves would have resulted, one corresponding to each spectrum, as explained above.





Group K elements—continuous line. Group L elements—points.



Group K elements—continuous line. Group L elements—points.

The results, as shown in the foregoing tables, can be stated as follows: Any particular radiation belonging to Group K, and having a certain penetrating power in aluminium, is absorbed by any other element, to the same extent as the radiation in Group L which has the same penetrating power in aluminium.

Further Considerations.

The evidence given does not yet completely establish the fact that the two series of radiations are identical in nature, though pointing in that direction. Owing, however, to the importance of the clearest proof of a property which depends on electronic structure, and which repeats itself in two elements of different atomic weights, it is essential that the comparative analysis of the two series of radiations should be carried further.

It has been proved that two radiations belonging to different groups, and having the same penetrating power in aluminium, are absorbed to the same extent in any other element. This energy which is absorbed is in the most general case (*i.e.* when the element absorbing is capable of emitting a characteristic radiation) spent in producing various types of radiation in the substance in which the absorption takes place. Some of these results are—

(1) Homogeneous radiation.
(2) Scattered radiation.
(3) Corpuscular radiation.
(4) Ionisation.

The intensity of the scattered and the homogeneous radiation is in general too feeble to determine, but the intensity of the ionisation and the corpuscular radiation, produced under suitable conditions, is well within the limits of measurement.

In order, therefore, to make a more thorough study of the radiations in the two groups, one method is to take two radiations, one from each group, both having the same penetrating power in aluminium and therefore, as the first part of the research proves, the same penetrating power in all substances, and allow these radiations to be equally absorbed in various elements or compounds, which may be either in the metallic or gaseous state. If then we can measure the amount of corpuscular radiation or the intensity of the ionisation produced under varying conditions by the absorption of these equal amounts of energy, evidence will be obtained showing whether the distribution of total energy is the same in the case of the two radiations.

When the radiations in the two groups are compared as regards their absorption in different elements, it is found that there is only one common value of the absorption coefficient for which radiations actually exist in both groups. These are bromine and bismuth.

Element emitting radiation.	λ/ρ in *Al* of radiation.	λ/ρ in *Cu* of radiation.	λ/ρ in *Ag* of radiation.
Br (Group K) ...	16·3	128·5	75·4
Bi (Group L) ...	16·1	126·7	72·9

These values, it will be seen, are well within the limits of experimental error, when account is taken of the somewhat difficult scattering correction which has to be made when dealing with the radiations of Group L.

If then we take the element bromine as representing Group K and bismuth as representing Group L, it is possible to examine in detail the radiations given by each, and evidence can be obtained of similarity or dissimilarity in the nature of the two radiations. Any results yielded by this examination can then be applied to the whole spectrum of radiations common to both groups. It is proposed to test these two typical radiations by determining:—

(1) Their power of producing corpuscular radiation in various substances.

(2) Their ionising power in various substances.

The remaining portion of the research therefore divides itself into measurements of corpuscular radiation and ionisation.

Experiments on the Corpuscular Radiation.

The ionisation chamber was of brass, 8 cm. in diameter and 2 cm. in length. Its ends consisted of thin parchment stretched on brass caps. The fitting of these caps was such that without disturbing the apparatus each end of the chamber could be reversed. The whole of the inside of the chamber was lined with paper, and a paper shield was placed on the electrode. A difference of potential of 200 volts between the electrode and the vessel was sufficient to produce saturation.

The method of the experiment was as follows. On one face of each of the parchment sheets forming the ends of the chamber, a sheet of very thin foil was deposited, this foil was copper in the first experiment and was of such a thickness that while not absorbing any considerable fraction of the fluorescent radiations of the hardness used in the experiment (bromine and bismuth radiations), yet no electrons produced at the back surface were able to penetrate to the front surface. The foil being deposited on the parchments which formed the ends of the chamber, the copper faces were first placed facing outwards, so that when a ray travelled through the chamber it traversed successively copper, parchment, the air in the chamber, parchment, copper. Under these conditions, neglecting the small amount of scattered and corpuscular radiation emitted by the parchment, the ionisation in the chamber was due to :—

(1) The direct ionising effect of the X-rays on the air.

(2) The scattered and fluorescent rays from the copper.

That is, since parchment is such an inefficient radiator and the factor (2) is small, the resultant ionisation is almost wholly caused by the direct action of the X-rays.

Now consider the effect of reversing the ends of the chamber, so that instead of having the parchment on the inside the two ends are now formed by the thin foil. In this case an X-ray passes successively: Parchment, copper, the air in the chamber, copper, parchment. The ionisation under these circumstances was caused by :—

(1) The direct ionising effect of the X-rays on the air.

(2) The scattered and fluorescent X-rays from the copper.

(3) The corpuscular rays from the copper.

The ionisation caused by the scattered and fluorescent X-rays is small, but in any case this factor counterbalances in the two parts of the experiments, for the absorption of the scattered and fluorescent radiation by the parchment is small. The difference in the ionisation in the two cases must be due to (3) the corpuscular rays from the copper, the other constituents

being common to the two experiments. Herein lies the excellence of this method, for by a simple mechanical device it was possible, by finding the difference in the ionisation in the two cases, to measure at once the ionisation caused by the corpuscular radiation from the copper.

Using this apparatus the energies of the radiations from bromine and bismuth respectively were first compared in intensity by their power of producing ionisation in air. Let us assume for the moment that the beams are of the same intensity as measured by their absorption in air. In the experiment equal amounts of energy of these two beams were then absorbed by the copper. The point to decide was whether equal absorptions of energy would yield the same amount of corpuscular rays, in other words, whether the energy which is absorbed is distributed in the same proportion in the two cases.

The results are given in tabular form.

Copper as Corpuscular Radiator.

Radiation exciting copper.		Ionisation in air + ionisation due to corpuscular rays from copper.	Ionisation in air.	Ionisation due to corpuscular rays from copper.
Exp. I.	Br (Group K)...	100	63	37
	Bi (Group L) ...	100	64	36
Exp. II.	Br (Group K)...	100	65	35
	Bi (Group L) ...	100	63	37

The same experiment was repeated using tungsten (Group L) in the place of copper (Group K) as the source of the corpuscular radiation. The tungsten was deposited by means of gum and chloroform.

Tungsten as Corpuscular Radiator.

Radiation exciting tungsten.		Ionisation in air + ionisation due to corpuscular rays from tungsten.	Ionisation in air.	Ionisation due to corpuscular rays from tungsten.
Exp. I.	Br (Group K)...	100	72	28
	Bi (Group L)...	100	71	29
Exp. II.	Br (Group K)...	100	72	28
	Bi (Group L)...	100	75	25

In each experiment from the final column in the tables it is seen that the intensity of corpuscular radiation produced by equal absorptions of the two radiations is the same.

It is interesting to consider upon what factors the intensity of the corpuscular radiation emitted by a plate, and measured by its ionising power in air, depends.

Let I_0 be the intensity of the beam exciting the corpuscular radiator, which, since the latter is thin, we can consider constant; let t be the transformation coefficient of X-radiation into corpuscular radiation, then with the usual notation, dE being the amount of energy converted into corpuscular energy in a layer of thickness dx and unit cross-section,

$$dE = tI_0 dx.$$

If we assume that half the radiation produced at any layer goes forward and half backward, travelling normally to the surface, the total intensity of corpuscular rays emerging from one side of the plate if λ is the coefficient of absorption of the corpuscular rays is:—

$$E = \tfrac{1}{2} tI_0 \int_0^\infty e^{-\lambda x}\, dx = \tfrac{1}{2}\frac{tI_0}{\lambda}.$$

If each corpuscle produces on the average n ions in the air, the total ionisation will be

$$S = \tfrac{1}{2} tI_0 n/\lambda.$$

Then, considering one surface of the radiator alone, for the bromine radiation, inserting suffixes which explain themselves,

$$S_{Br} = \tfrac{1}{2} t_{Br} I_{Br} n_{Br}/\lambda_{Br}.$$

And similarly for the bismuth radiation:—

$$S_{Bi} = \tfrac{1}{2} t_{Bi} I_{Bi} n_{Bi}/\lambda_{Bi}.$$

But the experiment has shown that when

$$I_{Br} = I_{Bi} \quad \text{then} \quad S_{Br} = S_{Bi}.$$

Therefore $$t_{Br} n_{Br}/\lambda_{Br} = t_{Bi} n_{Bi}/\lambda_{Bi};$$

i.e., $$t_{Br} = t_{Bi}; \quad n_{Br} = n_{Bi}; \quad \lambda_{Br} = \lambda_{Bi}.$$

That is, the bromine and the bismuth radiations, although belonging to different groups, have the following properties in common:—

(1) They are equally transformed into corpuscular radiation ($t_{Br} = t_{Bi}$).

(2) The corpuscles ejected by the radiations have the same ionising and penetrating power ($n_{Br} = n_{Bi}$; $\lambda_{Br} = \lambda_{Bi}$).

Ionisation Experiments.

The ionisation chamber was cylindrical in shape, 2 cm. in length and 7 cm. in diameter, and each end was of thin parchment. The whole of the inside was lined with paper so as to minimise corpuscular radiation.

In the experiment two vapours were used, one nickel carbonyl, in which the homogeneous radiation of the heavy element was excited by the radiations bromine and bismuth, and the other ethyl bromide, in which the characteristic radiation was not stimulated by these two radiations. The vapours were introduced by exhausting the ionisation chamber, and then from the bulb attached letting in the requisite amount of saturated vapour. The results obtained are shown below.

Nickel Carbonyl.

Radiation exciting vapour.		Ionisation in nickel carbonyl.	Ionisation in air.	$\frac{\text{Ionisation in nickel carbonyl}}{\text{Ionisation in air}}$.
Exp. I.	Br (Group K)...	100	8·9	11·2
	Bi (Group L)...	100	9·1	11·0
Exp. II.	Br (Group K)...	100	8·8	11·4
	Bi (Group L)...	100	9·1	11·0

Ethyl Bromide.

Radiation exciting vapour.		Ionisation in ethyl bromide.	Ionisation in air.	$\frac{\text{Ionisation in ethyl bromide}}{\text{Ionisation in air}}$.
Exp. I.	Br (Group K)...	100	12·7	7·9
	Bi (Group L)...	100	12·2	8·2
Exp. II.	Br (Group K)...	100	12·2	8·2
	Bi (Group L)...	100	12·5	8·0

Thus the ratio of ionisation in compound to ionisation in air has the same value whether bromine or bismuth is used as the exciting radiation. If we take ionisation in air to be a measure of the energy absorbed in the air, and therefore proportional to the energy absorbed in the vapour, which follows from the first part of the research, it is seen that the same proportion of the energy absorbed is converted into ionisation whether the energy is derived from the bromine or the bismuth radiation.

So that as regards the phenomenon of ionisation the two radiations, bromine and bismuth, although belonging to different groups, behave as though identical in type, thus again demonstrating a similarity in property of the radiations of the two groups.

Conclusions.

It may appear that more than sufficient evidence has been brought forward to prove that the two series of radiations, although arising from

different atoms, are identical in nature; but it is necessary to establish this beyond doubt. For it is agreed that the phenomenon of secondary characteristic radiation is connected with the electronic distribution in the atom. Therefore the fact that the two series of radiations are identical in nature proves that properties which are dependent on electronic structure repeat themselves in atoms of different elements containing different numbers of electrons, and in this way furnishes one of the clearest examples which the subject of X-rays affords, of the theory put forward by Sir Joseph Thomson, namely, that "we should expect the corpuscles in the heavy atoms to be arranged, as it were, in bundles, the arrangement of the corpuscles in each bundle being similar to the arrangement in the atom of some lighter element."

Suppose that, as previously suggested, the fluorescent X-radiation is produced by the electronic system in the atom settling down after that atom has ejected an electron or electrons as a result of the primary pulse passing over it. Taking, first, the case of the light elements in Group K, suppose in the simple case that the ejected electron is expelled from a bundle of a certain definite arrangement; then, as the atomic weight of the radiating element increases, the arrangement of the "bundles" alters, as well as their number, till eventually "bundles" with the same definite arrangement of electrons appear in an atom of higher atomic weight. Under these conditions two atoms differing in weight would, owing to their similarity in essential radiating structure, emit precisely the same type of fluorescent radiation. This is purely hypothetical, but it serves to show the type of explanation demanded to explain the fact that two atoms differing in respect of chemical and physical properties, as well as in the number of electrons they contain, should yet emit the same type of fluorescent X-radiation.

No relation between elements of different atomic weights emitting identical radiations can be found on the basis of Mendeléef's table.

Summary.

The radiations belonging to Group K and Group L respectively have been investigated as regards their X-ray properties. In this connection the absorption of the various radiations of both groups in copper, silver, and platinum has been found. In all cases it has been shown that if radiations from different groups suffer the same absorption in aluminium, then they are equally absorbed in any other element.

It will be seen that bromine and bismuth, though in different groups, emit radiations of equal penetrating power, so that as regards total energy absorption they are identical radiations. The intensity of the corpuscular

radiation produced in tungsten and copper and the ionisation resulting in ethyl bromide and nickel carbonyl, when equal amounts of energy of the two radiations were absorbed in the various substances, have been measured, and were found in each case to be independent of the radiator.

The results prove that these two spectra of radiations, Group K and Group L, are *identical in their nature*, as is shown by measurements on radiations in both groups which test—(1) their absorption in elements; (2) their power of producing corpuscular radiation; (3) their power of ionising. This suggests that the mechanism of production is the same, although the elements emitting the radiation differ widely in atomic weight.

I wish to express my best thanks to Sir J. J. Thomson for his interest and advice throughout this research.

The Synthesis of a Silicalcyanide and of a Felspar.

By J. Emerson Reynolds, M.D., Sc.D., F.R.S.

(Received October 23,—Read November 21, 1912.)

[Plate 1.]

In the course of an investigation which has occupied much time during some years the writer has obtained a considerable number of definite compounds including silicon and the nitrogen of diverse organic groups in direct chemical union. Several of these new substances resemble in composition and in their general relations certain well-known compounds of carbon with nitrogen, such as amides, imides, and nitriles, among them being a silicocyanogen group, SiN, in combination. The formation of such substances afforded complete proof that silicon has, like carbon, though in less degree, a marked affinity for trivalent nitrogen, even when the latter is associated with complex organic groups.*

* These substances have been described in detail in the 'Transactions of the Chemical Society' in the following papers:—"The Action of Silicon Tetrabromide on Thiocarbamide," 'Chem. Soc. Trans.,' vol. 51, p. 202; "The Action of Silicon Tetrabromide on Allyl and Phenylthiocarbamides," vol. 53, p. 854; "The Action of Ethyl Alcohol on the Compound $(H_4N_2CS)_8SiBr_4$," vol. 53, p. 868; "On Silicotetraphenylamide, *para*- and *ortho*-Silicotetratolylamides, *α*- and *β*-Silicotetranaphthylamides," vol. 55, p. 474. These compounds were the first of those obtained in which silicon is exclusively united with nitrogen and forming crystalline substances. "The Action of Substituted Phenylamines on Silicon Tetrachloride," vol. 61, p. 453; "On Silicodiphenyldiimide and Silicotriphenylguanidine," vol. 77, p. 836; "The Bromination of Silicophenylimide and -amide, and the

In the mineral kingdom no definite compounds of silicon with nitrogen have yet been met with; nor are they likely to be found at any part of the earth's surface to which water has easy access, as it is probable that any such substances would be very speedily decomposed in presence of moisture into silica and ammonia, or their derivatives. On the other hand, the existence of the great group of "alumino-silicates," which constitute so large a proportion of granitic and other similar rocks, affords clear evidence of the strong attraction of silicon for aluminium, which latter acts as an essentially trivalent element in its high temperature relations, and seems capable under such conditions of doing chemical work somewhat similar to that of nitrogen. These considerations raised the question whether some at least of the alumino-silicates may not be regarded as fully oxidised products of silicides of trivalent aluminium, somewhat analogous to SiN, which had been formed at high temperatures in the first instance below the oxidised crust of the earth. It is evident that such "nuclear" silicides should be obtained for study by the complete deoxidation of the corresponding native silicates, or by direct synthesis from the suitable elements. The first method was found to be impracticable in the most important cases, *i.e.* of alumino-silicates including alkali or alkaline earth metals. The application of the second or synthetic method has proved satisfactory, as it has led to the discovery of a substance of remarkable stability, provisionally named Calcium Silicalcyanide, and with which a new synthesis of the felspar Anorthite has been effected. The results recorded in the following pages tend to support the view suggested above as to the nitrogen *rôle* of aluminium in certain silicides, and afford some further clues to the constitution and natural relations of the plagioclasic felspars.

Experimental Part.

The *reduction*, or deoxidation, of silica and alumino-silicates is easily effected by several agents; but the most convenient of these is metallic magnesium. It is well known that the finely divided metal when heated with silica (SiO_2) in suitable proportions readily removes all the oxygen of that substance, so that elemental silicon and magnesium oxide result, and the latter can then be removed by hydrochloric acid, in which silicon is insoluble. All the "alumino-silicates" which I have treated in the same manner are also reduced, but not completely; for example, anorthite,

formation of a Compound including the Group SiN," vol. 87, p. 1870; "On Interactions of Silicotetraphenylamide and Thiocarbimides," vol. 88, p. 252; "On Silicon Thiocyanate: its Properties and Constitution," vol. 89, p. 397; "On Silicotetrapyrrole," vol. 95, p. 505; "The Action of Potassium-pyrrole on Silico-chloroform," vol. 95, p. 508; and "Silicon Halides with Pyridine, Acetonitrile, etc.," vol. 95, p. 513.

oligoclase, orthoclase, and scapolite, when heated with the proportion of magnesium suitable for the removal of the whole of the oxygen in each case, gave nearly black reduction products. These were closely examined and found to be slightly coherent masses which did not afford any metal-like particles when broken up. Treated with cold water, no gas was evolved, and very little even on boiling; but the alkalies present in any of the minerals were not deoxidised, and dissolved in the water, along with much of the lime from anorthite and scapolite. The alkaline substances were washed away and the black insoluble residue, which still contained magnesia but no visible traces of metal, was in each case treated with hydrochloric acid; some hydrogen was given off, and the colour of the powder changed to the well-known brown of finely divided and amorphous silicon, while aluminium and magnesium passed into solution.

In all these cases it was evident that the chief effect was reduction to silicon with more or less of a black silicide of aluminium, which latter was subsequently decomposed by the acid—a further proportion of silicon separating. The reduction method, therefore, only partially attained the end in view; hence, attention was next given to the second line of treatment.

The *synthetic* method consisted in attempts to combine the unoxidised elements under well defined conditions, and to study any definite products obtained.

On the hypothesis already suggested, that aluminium can, in certain cases, act in regard to silicon in inorganic nature much as nitrogen does to carbon in the organic division, we should expect the following series of compounds to exist:—

Cyanogen	C_2N_2 or $(CN)_2$
Silicocyanogen	Si_2N_2 or $(SiN)_2$
Silicalcyanogen...........	Si_2Al_2 or $(SiAl)_2$

We know that the first term of this series—ordinary cyanogen gas—is formed with difficulty from its elements except at very high temperatures, but much more readily in presence of a third and more positive substance, such as an alkali metal, which can directly combine with cyanogen as it is formed and produce a cyanide. The second term is not known in the free state, unless it is the white substance which is produced when silicon is heated to the temperature of the electric arc in an atmosphere of nitrogen; but I have obtained the group SiN in organic combination. The third term has not been recognised hitherto either in the free state or in combination. It seemed probable, however, that Si_2Al_2 might be more easily formed by direct union of the elements than the others, because both are fusible solids; hence the first experiments were directed to this point.

It is well known that silicon dissolves freely in molten aluminium at moderately high temperatures, but that much of the former separates in crystals on cooling. Winckler found that when the liquid from which excess of silicon had crystallised out and been removed was allowed to solidify, it consisted of nearly equal parts of silicon and aluminium. As the atomic weights of the elements are Si = 28·3 and Al = 27·1, Winckler* was disposed to regard this "alloy" as a definite compound, and therefore to be represented by the formula SiAl. On the other hand, Vigouroux† denies that any definite compound is formed when aluminium and silicon are fused together. Fraenkel,‡ also, concludes from his thermochemical observations that there is little or no chemical combination. The following experiments were made with a view to examine this point more closely.

100 grms. of the purest commercial aluminium were fused in a "salamander" crucible, and 104 grms. of graphitic silicon were added in small fragments to the molten metal. There was no evidence of chemical action after each addition nor as the silicon slowly dissolved. When complete solution was obtained the liquid was heated to full redness for half an hour, and the crucible with its contents were then allowed to cool slowly. An apparently homogeneous grey metallic mass was broken out of the crucible which had but slightly oxidised at the surface exposed to the air. A horizontal section made through the middle of this mass showed that the bright metallic surface was crossed by numerous long crystals. A section of about a centimetre in thickness was half immersed in much diluted hydrochloric acid for a day, and deep etching was obtained owing to solution of aluminium. The long crystals which were left in relief, as shown in fig. 1, were found to consist of silicon only. It will be seen, however, that a few crystalline and brilliantly reflecting plates are present in addition to the silicon crystals. Some of these plates were carefully picked out and treated with much stronger acid than that used in etching; the plates disintegrated, leaving pulverulent silicon, while aluminium dissolved. These plates probably represent traces of combination between the two elements.

I next sought to ascertain the composition of the material in which the silicon crystals were embedded. For this purpose a moderately thin section of the large mass, weighing some 30 grm., was supported on edge in a bath of melted calcium chloride, which fuses between 717° and 723° (Carnelly), or a little above the melting point of aluminium, *i.e.* about 700°. Gradual liquation of the aluminium occurred and much crystalline silicon was left. When cold

* 'Journ. für Praktische Chemie,' vol. 91, p. 193.
† 'Comptes Rendus,' vol. 141, p. 951.
‡ 'Zeits. für Anorg. Chemie,' 1908, vol. 58, p. 154.

the metal-like product resembled aluminium in colour but was quite crystalline in structure throughout. The composition proved to be—

Silicon	28·33
Aluminium	71·57
	99·90

This product when treated with acid also left crystals of silicon.

The original mass contained 50·8 per cent. of silicon, and a portion of this when remelted and suddenly cooled gave a good ingot which was steel-grey in colour, and the fractured surface presented the minutely crystalline structure shown in fig. 2. A portion of the same ingot was again fused and maintained at a full red heat for nearly two hours and then slowly cooled as in the first instance. A section of this product when etched presented much the same appearance as in fig. 1, save that the plates already referred to seemed to be rather more numerous, as if the prolonged fusion had promoted a little further combination of silicon with aluminium.

It is evident that silicon and aluminium do not directly enter into chemical combination to any material extent, even when a liquid mixture in atomic proportions is heated to full redness for more than two hours. Under similar conditions carbon and nitrogen do not evince any greater tendency to unite and form cyanogen; but, in the latter case, if a third element be present, such as an alkali metal, then combination takes place and a cyanide of the metal is formed. On the "silicalcyanogen" hypothesis I have suggested, the addition of an alkali metal, or its equivalent, to the fused alloy of silicon and aluminium should act in a similar manner and lead to the formation of a silicalcyanide of the metal.

A number of prospecting experiments were next made with the molten alloy of silicon and aluminium in atomic proportions, in which sodium, potassium, magnesium and calcium were added to separate parts of the fused alloy. The alkali metals proved to be much too volatile for use in open crucibles*; magnesium dissolved quietly in the alloy without affording much evidence of chemical combination either in process or product; but calcium caused almost violent action as it dissolved in the SiAl alloy, and afforded a very characteristic product. Further experiments having indicated the best conditions for a preparation on a comparatively large scale, this was made in the following manner:—

100 grms. of the purest aluminium obtainable in commerce were fused in a relatively large-sized crucible, heated in a powerful gas blast furnace;

* It will be shown later on that in closed vessels union can be effected to a certain extent.

103 grms. of crystalline silicon, as free as possible from carbide, were introduced, and the heat was continued until complete liquefaction was obtained; 74 grms. of metallic calcium, cut into small pieces, were then gradually added to the molten alloy; each piece, when pressed under the surface of the liquid, caused energetic action, and after the latter had somewhat subsided the liquid was well stirred with a steel rod. Owing to this frequent stirring it was easy to note that the mass became sensibly less fluid after the addition of about half the calcium, as if owing to the separation of less fusible material, and this thickening increased until the last addition was made, when it became nearly solid.* The temperature was then raised to the highest point attainable during half-an-hour, but without fusion, and the whole was then allowed to cool very slowly.

When cold the crucible was broken away and a clean metal-like mass of a dark grey colour was extracted. This weighed 279 grms.—the small increase in weight, about 2 grms., being doubtless due to some oxidation during the vigorous interaction which took place on the addition of the calcium. All traces of free aluminium had disappeared.

A vertical section through the mass presented smooth metal-like surfaces with markings indicative of crystal sections, and the material, which could be easily broken up by a hammer, presented a highly crystalline structure and seemed to be uniform in character. The brilliant crystalline faces appeared to belong to octahedral forms, and to be of the same kind throughout the mass; but at certain parts a dark powdery substance was found which evidently consisted of the mixed oxides already referred to, as having been formed in small quantity at the surface, and then become entangled during the final stirring of the somewhat thick alloy; this powder, which owed its dark colour to mixture with the finely divided portions of the alloy, was easily brushed away, and the broken product then presented the appearance shown in fig. 3.

Some of the best defined crystalline groups were taken from different parts of the mass and their densities determined at 16° in water, which does not sensibly act on the alloy at ordinary temperatures, unless after long contact.

Upper section	2·347
Middle „	2·351
Lower „	2·353

As the densities of the constituents varied between 2·71 for aluminium and 1·534 for calcium, there had not been any material separation, so confirming the essentially homogeneous character of the "alloy."

* The proportion of calcium added was then nearly $Ca : Si_2 : Al_2$.

Notwithstanding the above evidence, and the known weights of the elements used in the preparation of the alloy, analysis was considered desirable, hence rather large portions were broken from about the middle of the mass; these well crystallised specimens were brushed free from scoria and then finely powdered. The method of analysis consisted in heating the substance, spread in a thin layer on a porcelain boat contained in a Jena glass tube, in a current of carefully dried chlorine gas. The powder was soon attacked and the constituents were converted into chlorides; calcium chloride, not being volatile, was left in the boat when aluminium and silicon, as chlorides, were volatilised by heat and the vapours wholly absorbed by water; Si and Al were then separated in the usual manner. The results of two analyses so conducted are given below, and are compared with the composition of a compound consisting of $CaSi_2Al_2$.

	Theory.	I.	II.
Silicon	37·63	36·81	36·76
Aluminium	35·92	—	35·8
Calcium	26·45	25·72	25·86
	100·0		

The slight oxidation which occurred during the preparation of the substance, as already explained, is doubtless the chief cause of the lower values obtained for silicon and calcium than those required by the formula.*

The indifference of this substance to oxygen, even at comparatively high temperatures, is as remarkable as its infusibility. In a special experiment, 2 grms. of the metal-like material, in a rather finely powdered condition, were strongly heated in a porcelain boat placed in a hard glass tube, through which a current of dry oxygen was passed for an hour, while the temperature was maintained as near as was safe to the softening point of the containing tube. The powder did not fuse, and was very slightly altered in appearance; when cold it was found to have gained only 0·08 grm. in weight. When heated in air by the oxyhydrogen flame, the "alloy" melts, and immediately bursts into vigorous combustion, affording a white semi-fused product.

The substance is also remarkable in that water acts very slightly upon it at ordinary temperatures, and little more if boiling, thereby proving

* Numerous silicides and alloys, including aluminium and other elements, have been formed, and are described in the elaborate treatise of M. Baraduc-Muller, 'Sur les Siliciures Metalliques' (Angers, 1910, 4to), but no "alloy" resembling the above either in composition or properties appears to have been obtained.

incidentally that the large proportion of calcium which is present is wholly in chemical combination. It is readily attacked, and in part dissolved, by hydrochloric acid, with evolution of hydrogen silicide and free hydrogen, while much silicon separates, aluminium and calcium passing into solution. Strong nitric acid is almost without action in the cold, but the boiling acid slowly attacks the substance; sulphuric acid has little action even when hot. On the other hand, sodium and potassium hydroxides in strong solution act readily in the cold and rapidly on boiling. When dry chlorine is passed over the substance, action begins without the application of external heat, and the products are calcium, aluminium, and silicon chlorides. Advantage was taken of this complete action in order to effect the analyses given above.

The substance presents the essential characters of a chemical compound, and appears to be one which has been formed from its elements much in the same manner that a metallic cyanide can be synthesised, silicon and aluminium representing carbon and nitrogen.* The analogy with a cyanide is easily recognised when the respective formulæ are written as under :—

$$Ca\begin{matrix}\diagup CN \\ \diagdown CN\end{matrix}\ , \qquad Ca\begin{matrix}\diagup SiAl \\ \diagdown SiAl\end{matrix}\ .$$

Calcium cyanide. Calcium salicalcyanide.

It has been mentioned above that calcium silicalcyanide is very slightly attacked by free oxygen until the temperature of the oxyhydrogen flame is reached. I may add that even fused potassium chlorate produces little effect upon it, and fused nitre is partial in its action. If heated with easily reduced metallic oxides, such as lead oxide, the compound is broken up, and a lead, calcium, and aluminium glass results from secondary changes.

There is no doubt, however, that the crystalline $Ca(SiAl)_2$ is capable of combining with eight atoms of oxygen, and of producing therewith a compound of the same composition as the mineral anorthite, that is $CaSi_2Al_2O_8$. Now, ordinary cyanides of alkali or alkaline earth metals are by no means easily affected by gaseous oxygen even at comparatively high temperatures, but, if water vapour be present along with oxygen, change takes place at comparatively low temperatures, resulting in the formation of a carbonate of the metal, while ammonia is formed and separated.† Such a change effected in the case of calcium cyanide can be represented in the following manner :—

$$Ca\begin{matrix}\diagup CN \\ \diagdown CN\end{matrix} + O_2 + 3H_2O = CaCO_3 + 2NH_3 + CO_2.$$

* It is possible that barium and strontium may give similar products.

† Unless oxygen is present in excess, when ammonia is oxidised in its turn.

The silicalcyanide should obviously be capable of somewhat similar hydrolytic oxidation, and that proved to be the case, although the inability of aluminium to form a volatile compound like ammonia necessarily led to a modification in the nature of the end product. After several trials the most convenient mode of effecting the change proved to be the following:—

About 2 grms. of the finely powdered alloy were placed in a Rose crucible of rather large size with the usual perforated cover and clay delivery tube for conveyance of gas to the interior. The tube was connected with a flask containing water through which a stream of oxygen was allowed to bubble on its way to the crucible. By heating the water in the flask the proportion of water vapour carried along with the gas could be increased at will, and heating the clay tube prevented condensation before the hot crucible and its contents were reached. Under these conditions the moist oxygen led over the powder, which was heated to low redness, gradually converted it into a nearly white mass. Two successive quantities were treated in the same manner until sufficient of the white product was obtained; the whole was then powdered, returned to the crucible, and again strongly heated in the current of moist oxygen until perfectly white. This material proved to be infusible at the highest temperature attainable in a small gas blast furnace; but when an oxyhydrogen flame was made to impinge on the surface complete fusion was effected of the greater part of the mass; much care was taken to avoid fusing the material of the crucible as well. When slowly cooled in order to permit crystallisation the surface presented the somewhat volcanic appearance shown in fig. 4. Under the crater-like top a good proportion of solid and highly crystalline substance was found.

The best crystallised portions of this product from calcium silicalcyanide were picked out for examination and analysis. When compared with a specimen of opalescent anorthite from the Tyrol my synthetic product proved to be very similar in character, and it was gelatinised by acids in much the same way.

0·962 grm. gave 0·3996 grm. of SiO_2, 0·3615 of Al_2O_3, and 0·2045 of CaO.

These data lead nearly to the ratios

$$CaO : Al_2O_3 : 2SiO_2 = CaAl_2Si_2O_8,$$

or those of the mineral anorthite.

Mr. Herbert H. Thomas, of H.M. Geological Survey, has been so good as to examine a specimen of this product, and kindly allows me to quote his observations, as follows:—"In thin section it presents the appearance of a mass of acicular crystals which radiate from a series of centres; the

individual needles are twinned once in most cases, but in some instances it was possible to make out polysynthetic lamellæ.

"The powdered mineral has a mean refractive index of about 1·582 and a specific gravity of about 2·75 to 2·76 (heavy liquid method).

"The mineral has low birefringence, large extinction angle on the plane of the best cleavage, and is most certainly a felspar. The high mean refractive index and specific gravity both point with certainty to anorthite."

In the following table the percentage composition of my synthetic* anorthite is compared with theory for the pure substance, and with analyses of native specimens, in order to show the range of variation in composition. For convenience of comparison all the monoxides present in the native minerals have been calculated into their equivalents of CaO and added to the percentages of the latter which were actually obtained. No. 1 is of clear crystals from Monte Somma, analysed by Abich. No. 2 is of the massive variety indianite. No. 3 is of the variety named barsowite, analysed by Friederici:—

	Theory.	No. 1.	No. 2.	No. 3.	New synthetic.
SiO_2	43·08	43·96	42·09	41·56	41·53
Al_2O_3..............	36·82	35·72	38·89	36·59	37·3
CaO	20·1	20·26	19·46	21·42	21·25
	100·0				

Whether formed by partially hydrolytic action at comparatively low temperatures, or by direct oxidation alone at much higher temperatures, the relations of calcium silicalcyanide and anorthite are simple, and are expressed in the constitutional formula for the mineral given below:—

$$\mathrm{Ca}\begin{cases}\mathrm{Si}\equiv\mathrm{Al}\\ \mathrm{Si}\equiv\mathrm{Al}\end{cases} \quad : \quad \mathrm{Ca}\begin{cases}\mathrm{O{-}SiO_2{-}Al{=}O}\\ \mathrm{O{-}SiO_2{-}Al{=}O}\end{cases}.$$

Calcium silicalcyanide. Anorthite.

If nitrogen were present in the unoxidised compound instead of aluminium then hydrolysis would have involved its removal as NH_3 gas, and the residue would probably have been a calcium disilicate, which is a potentially acid salt. Anorthite is, on the contrary, a markedly basic silicate, because aluminium does not form any such gaseous compound as NH_3, and in

* The synthesis of anorthite has been effected from the oxides or other compounds of the component elements, but this one is obviously different in character from those which preceded it.

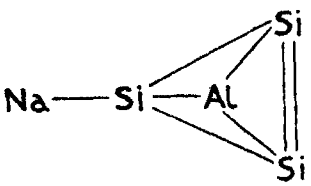
presence of an excess of oxygen, is retained in the molecule as a distinctly electropositive constituent. It is probably owing to the essentially basic character of anorthite that it is so rarely found in the pure state.

According to Tschermac's well-known view, all the plagioclasic felspars are either isomorphous mixtures, or solid solutions, of basic anorthite and the acidic felspar albite in various proportions. These transition minerals are the important rock formers—labradorite, andesine, and oligoclase, with other minor varieties, which exhibit well known and gradual changes in chemical composition and in physical characters between the two extremes.

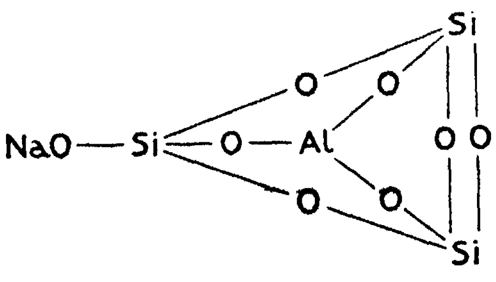
Notwithstanding the wide difference in composition between anorthite and albite, which becomes apparent when the simplest expression of the composition of each mineral is compared as under—

Anorthite	$CaSi_2Al_2O_8$
Albite	$NaSi_3AlO_8$

their known relations above mentioned indicate that there is some fundamental similarity in constitution. If the unoxidised nuclei are considered in view of the information gained in the earlier part of this work, it is easy to trace such a relationship. The simple silicalcyanide type underlying anorthite is —SiAl; that of albite is obviously more complex, but still includes at least one such member, if the nucleus be represented by the following constitutional formula :—



Ultimate oxidation of this to albite probably would not make any material change in the relations of the principal elements, and the constitution of that mineral may similarly be represented as under—



It is probable that the free molecule of albite should be represented by two

such groups* linked up by the residual valence of aluminium. Orthoclase, KSi_3AlO_8, may be similar in structure.

The synthesis of albite from the oxides of its component elements is well known to be attended with difficulty; but the synthesis of the corresponding silicide is still more difficult,* owing to the volatility of sodium, and heating under pressure in presence of a considerable excess of sodium is necessary. When the requisite materials were heated in a strong iron tube, closed by a tightly screwed cap, some combination was effected. This tube and its contents, placed in an inclined position in a powerful muffle furnace, was heated to the highest attainable temperature for nearly two hours, and then allowed to cool in sand; when quite cold it was cut into four pieces of nearly equal length. The upper part was lined by some condensed sodium; the next section contained some sodium also, and the third section was found to contain a grey metal-like mass. This was somewhat crystalline in character, quite hard enough to require the use of a chisel in order to cut it out, but the material easily took fire on friction, and when thrown into water gave abundance of hydrogen gas and a little hydrogen silicide. A portion of the grey crystalline alloy was picked out in as clean a condition as possible, and was found to contain silicon, aluminium, and much sodium. It is probably a solid solution of $NaSi_3Al$ in sodium. The lowest section of the tube contained more of the grey alloy and a little free silicon. This alloy is the nearest in the way of an unoxidised albite nucleus that I have as yet been able to obtain.

It is evidently possible that somewhat similar relations may be traceable between alumino-silicides of other types and other classes of "alumino-silicates."

Much of the work recorded in this paper was carried out in the Davy-Faraday Laboratory, and my grateful acknowledgments are due for the facilities afforded by that institution.

* Some chemists, including Deville and Vigouroux, were unable to secure the combination of silicon with sodium or potassium under any conditions; but Moissan, in 1904, easily effected superficial combination by passing the vapour of sodium over silicon at high temperatures.

Fig. 1.

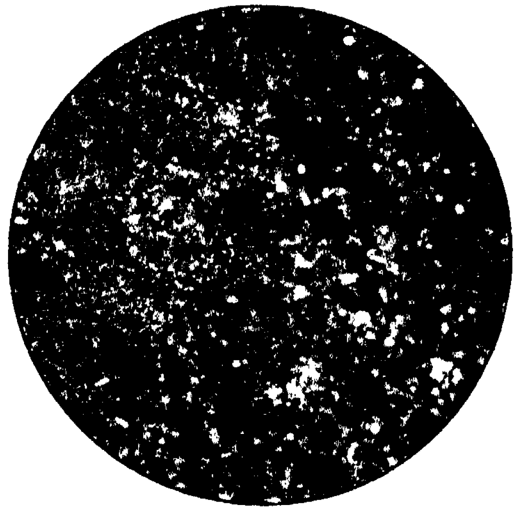


Fig. 2.

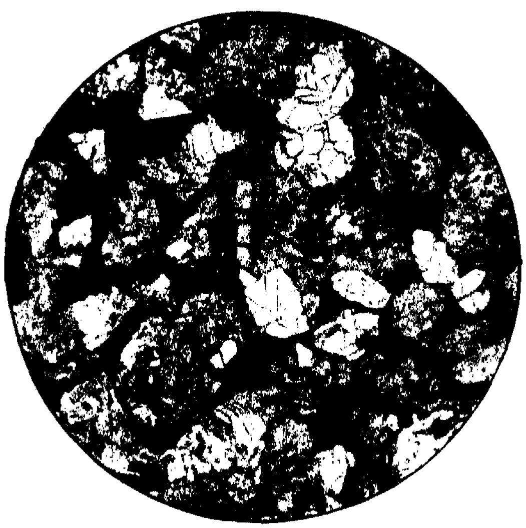


Fig. 3.

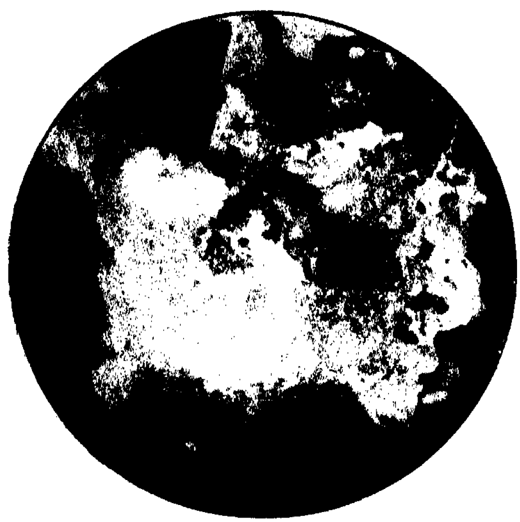


Fig. 4.

A Determination of the Radiation Constant.

By H. B. Keene, B.Sc., Assistant Lecturer in Physics in the University of Birmingham.

(Communicated by Prof. J. H. Poynting, F.R.S. Received November 7,—Read December 5, 1912.)

According to the Stefan-Boltzmann law, the radiation emitted by a full radiator in surroundings at a temperature of absolute zero is proportional to the fourth power of the absolute temperature of the radiator, or $R = \sigma\theta^4$, where R = radiation in ergs per cm.^{2} per sec., θ = absolute temperature of radiator, σ = radiation constant. If the radiator is in surroundings at absolute temperature θ_1, which are themselves full radiators, then

$$R' = R_\theta - R_{\theta_1} = \sigma(\theta^4 - \theta_1{}^4),$$

where R' is the net radiation.

The first important determination of the radiation constant is due to Kurlbaum,* who obtained a value $5{\cdot}33 \times 10^{-5}$ erg/sec. cm.^{2} deg.^{4}, recently corrected to $5{\cdot}45 \times 10^{-5}$ erg/sec. cm.^{2} deg.^{4}.† Later investigations give results varying considerably from Kurlbaum's and from one another, and, on the whole, they indicate that Kurlbaum's value is too low. Some determinations are given in the following table:—

Observer.	Date.	$\sigma \times 10^5$.
Kurlbaum	1898	5·45
Féry	1909	6·30
Bauer and Moulin	1909	5·30
Valentiner	1910	5·47
Féry and Drecq	1911	6·51
Shakespear	1912	5·67
Gerlach	1912	5·80

The essential conditions in a determination of σ are, either that both emitter and receiver are full radiators, or that the amount by which they fall short of full radiators is known—an amount difficult to determine with certainty.

Hitherto, a measurement of σ in which both emitter and receiver were full radiators has not been made. Féry‡ and Féry and Drecq§, who have

* 'Ann. d. Phys.,' 1898, vol. 65.
† 'Ann. d. Phys.,' May, 1912.
‡ 'Compt. Rend.,' April 5, 1909.
§ 'Journ. d. Phys.,' July, 1911, p. 558.

obtained results $6{\cdot}3 \times 10^{-5}$ and $6{\cdot}5 \times 10^{-5}$ erg/sec. cm.^{2} deg.^{4}, used a blackened conical receiver, which is more nearly a full receiver than a plain black surface. Féry has pointed out that the advantage of this receiver depends upon the large number of reflections made by the incident radiation within the cone. At all points of incidence and reflection, diffusion, as well as reflection, takes place, which implies energy losses from the mouth of the cone. In this respect the instrument used by Féry is not a full receiver.

The nearest approach which we can make in practice to a full radiator or receiver consists in a good radiating surface in the form of a uniform temperature enclosure, with an aperture small compared with the total internal area.

The present paper describes some experiments in which the receiver fulfilled the above conditions. The emitter could only be considered an approximation to a full radiator. It consisted of a small Heræus furnace at a temperature of about 1000° C. The construction of such a furnace does not lend itself to the production of a perfectly uniform temperature enclosure. Steps taken to improve the furnace in this respect will be described later.

One of the chief objects of the paper is to describe the full receiver and to show that it is capable of giving consistent results. At present a furnace is being constructed which approximates more nearly to the ideal full radiator and it is intended to make further measurements with it when completed.

For the purpose of the experiment it is necessary to calculate the energy exchange between two fully radiating coaxial circular apertures at different temperatures, and at a distance apart of the same order as the diameters of the apertures themselves. This calculation is given in the appendix, where it is shown that

$$E = \tfrac{1}{4}\pi R' (r_1 - r_2)^2,$$

where E is rate of emission of energy from one of the apertures, R′ is net radiation per cm.^{2}/sec, r_1 and r_2 the greatest and least distances between two points, one on each circle bounding the apertures.

In order to bring this expression into line with that used when the distance between the apertures is large compared with their diameters, it may be written

$$E = R' s_1 s_2 \{1 - (a^2 + b^2)/D^2\} / \pi D^2$$

as a first approximation, where s_1, s_2 are the areas of apertures; a, b, the radii of apertures; D, the distance between apertures.

If a and b are small compared with D, then the expression takes the familiar form in which it has been used by those investigators who have confined themselves to such distances that the correction $\{1 - (a^2 + b^2)/D^2\}$ was negligible.

In the arrangement to be described this expression was of the order 0·98, the radiation constant being calculated from the expression

$$E = \sigma\theta^4 s_1 s_2 \{1-(a^2+b^2)/D^2\}/\pi D^2,$$

where σ is the radiation constant and θ is the absolute temperature of furnace. The fourth power of the absolute temperature of the receiver was negligible in comparison with that of the furnace.

Description of Apparatus.

The receiver consisted essentially of an aniline thermometer with a bulb of about 2 litres capacity and a stem of 1 mm. bore. The bulb had double walls, between which was the aniline, the inner hollow cavity being lamp-blacked and provided with a circular orifice A which served as the receiving

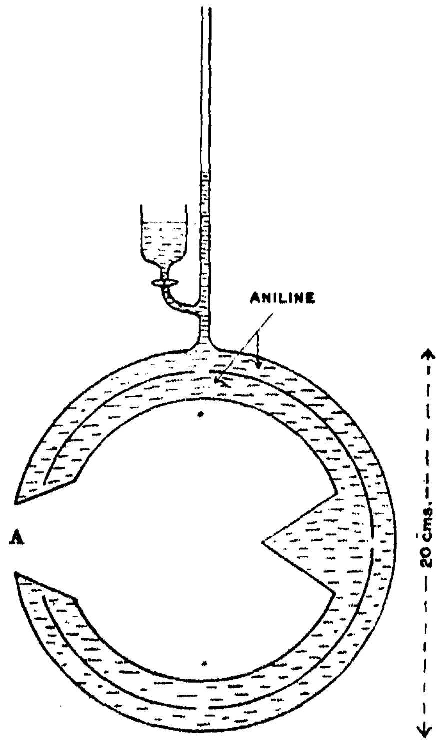


FIG. 1.

aperture (see fig. 1). The bulb was constructed of thin spherical copper shells, the inner one being 15 cm. in diameter, with an aperture of about 2 cm.². A third copper shell was placed in the liquid between the inner and outer shell to serve as a screen to prevent initial heat losses by direct radiation through the aniline from the inner surface. Radiation from the

furnace aperture was received by the aperture A (fig. 1), and fell on the inner blackened surface at the back of the bulb. In order to minimise energy losses by direct reflection, this region was occupied by a thin copper cone, so that no part of the receiving surface received rays normally. Since the thermometer contained a badly conducting liquid and also a screen to prevent radiation losses to the outside, the initial march of the meniscus in the stem gave a measure of the energy received per second; 1 mm. rise of the meniscus corresponded to a rise of temperature of 0·0005° C. In order to eliminate the effect of external temperature variations a companion thermometer was constructed, and both thermometer bulbs were enclosed in

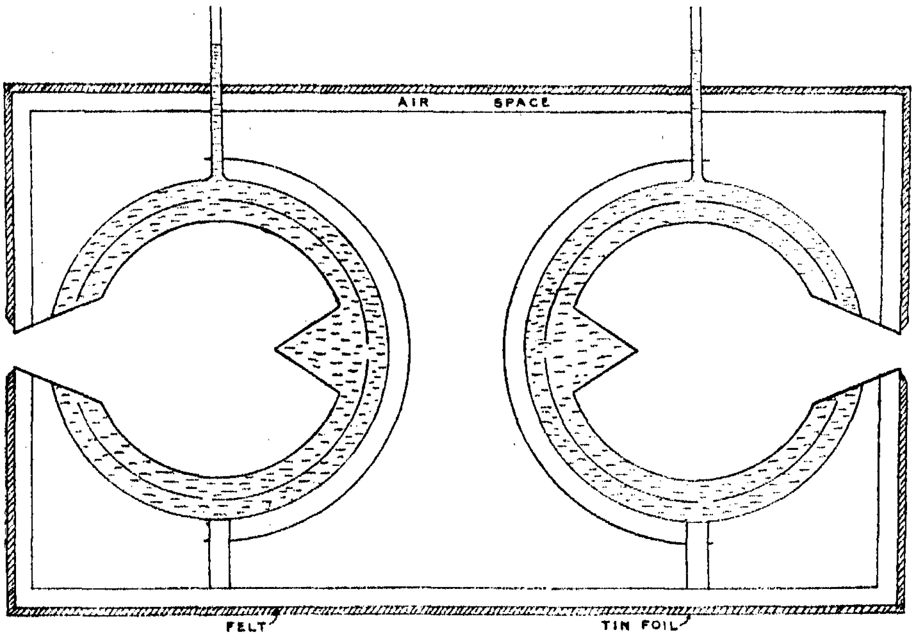


Fig. 2.

the same heat-insulating jacket, one alone receiving energy from the emitter. The jacket consisted of a double-walled zinc box well lagged on the outside with felt, the outer surface of which was covered with bright tinfoil (see fig. 2). In this way the rate of change of temperature of the two thermometers was made as small as possible when the room temperature was changing. The thermometers were now used differentially, allowance being made for the small difference in capacity and bore of capillaries. The march of the two meniscuses was observed prior to admitting radiation from the furnace into one of the apertures, and when the room temperature was changing slowly and uniformly, a screen was removed and the radiation

was admitted. The observations were now continued every half minute for 12 minutes, and the differential effect due to the energy from the furnace alone was determined.

The emitter consisted of a cylindrical electric furnace of the Heræus type, about 3·5 cm. in diameter and 20 cm. in length. Owing to the low conductivity of the porcelain tube on which was wound the platinum heating strip considerable temperature differences, visible to the eye at red heat, exist between each successive turn of the heating spiral. These differences were minimised by the introduction of a lining cylinder of nickel and two nickel plugs near the centre of the furnace (see fig. 3). In spite of this precaution a considerable fall of temperature takes place from the centre of the furnace to the aperture, and although the extremity of this region near

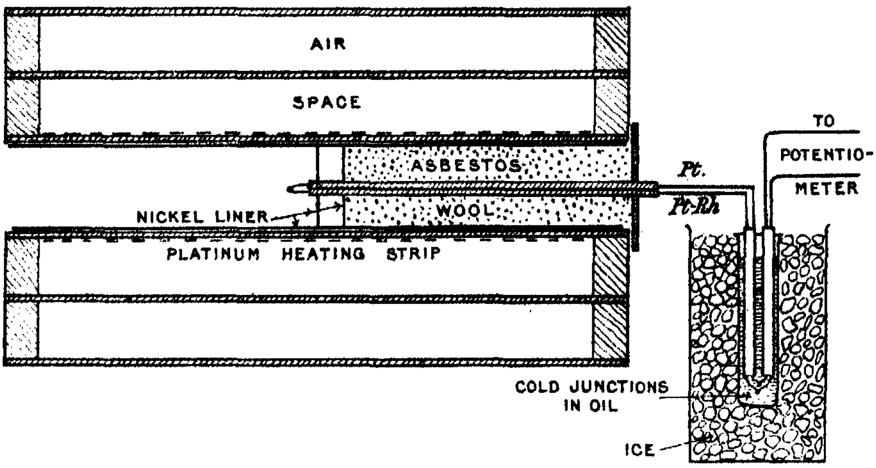


Fig. 3.

the aperture is not visible from the receiving aperture, such an enclosure does not constitute a full radiator. For this reason the results of the present measurements are offered as preliminary observations pending the construction of a new high temperature full radiator.

Screens.—Between the emitting and receiving apertures were two water-cooled screens coated with paraffin black on their surface (see fig. 4). In order to avoid heating of the furnace screen by the furnace a continuous stream of cold water from the town mains was brought in at the centre of this screen and conducted by means of a spiral guide to the extremities. To ensure an even flow of water through the screen placed before the receiver, the water was brought in at a number of peints at the bottom of the screen and taken out in a similar way at the top. The aperture in each screen consisted of a blackened cone of thin spun copper.

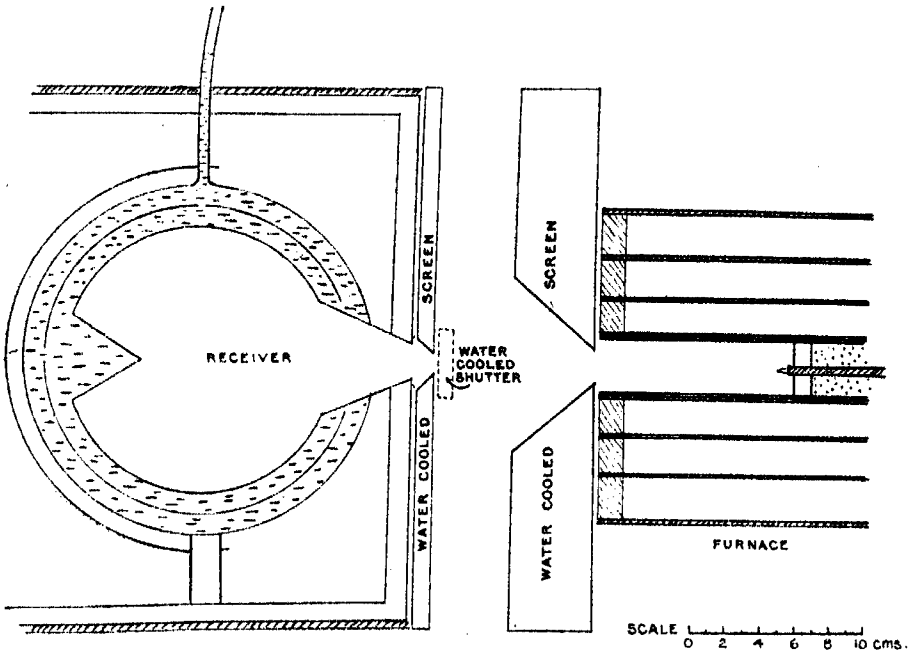


Fig. 4.

Method of Carrying out a Measurement.

(1) *Calibration of Receiver.*—The receiver contained a bare insulated platinum wire attached to the inner surface by a number of glass hooks.

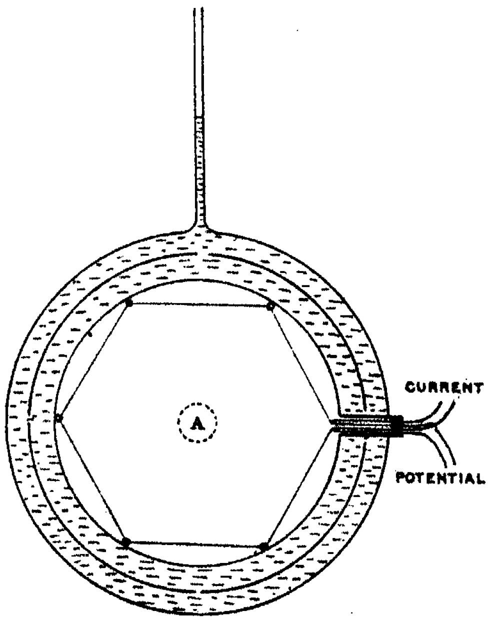


Fig. 5.

The wire formed a polygon lying close to the inner surface of the receiver; the plane of the polygon was symmetrically placed within the sphere and occupied a position parallel to the plane of the receiving aperture. The wire was provided with current and potential leads, and served as a means of introducing electrical energy for the purposes of calibration (see fig. 5).

The calibration was carried out as follows: When the apparatus indicated that the room temperature was changing slowly and uniformly the electric

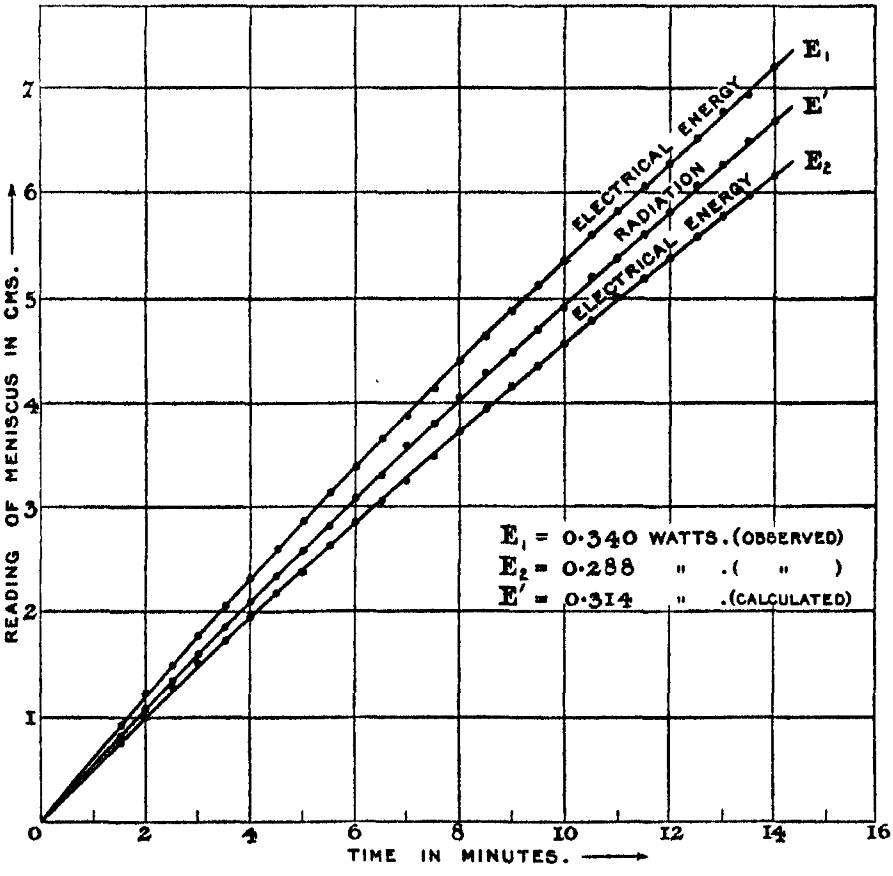


Fig. 6.

circuit was completed at a noted instant. The march of the meniscus both of the thermometer containing the electric circuit and of the companion thermometer was now observed every half-minute for 12 minutes. These readings were plotted against time, and the differential effect due to the energy received from the wire alone was determined. Two actual curves are shown on a reduced scale in fig. 6. By varying the electrical energy

a series of such curves was obtained (E_1, E_2, fig. 6). It was found that the ordinates of the successive curves at a given time t after the circuit was completed were proportional to the given energy supplies. This was true whatever the value of t, except at the beginning of the curves, where slight irregularities were apparent.

Twenty-four hours were allowed to elapse between each experiment. This was found to be necessary in order to allow both thermometers to come to the same temperature conditions.

(2) *Measurement of Energy Stream.*—Similar curves were obtained when energy was received by radiation from the furnace. Such a curve is shown at E′, fig. 6. The energy per second corresponding to the curve E′ could be readily obtained by interpolation from the neighbouring calibration curves. The initial portions of the curves were discarded and interpolations carried out at each of four successive different values of the abscissæ, viz., after 5, 8, 10, and 12 minutes, and the mean value taken.

Before the admission of radiation to the receiver from the furnace, the latter was allowed to run for four hours in order that it might reach a steady state. During this time a water-cooled zinc diaphragm was in position immediately in front of the receiving aperture. This screen, indicated by the dotted rectangle in fig. 4, consisted of a flat cylindrical box 4 cm. in diameter and 1 cm. thick, and carried a stream of running water at room temperature. Both sides of the screen were coated with paraffin black. When the furnace had attained a steady temperature, as indicated by the thermocouple within, the water-cooled diaphragm was swung out of position at a noted instant and the march of the meniscuses observed as already described.

(3) *Temperature of Furnace.*—This was measured by a platinum-platinum-rhodium thermocouple and potentiometer, the maximum error being from 1° to 2° in the neighbourhood of 1100° C. After use the couple was calibrated at the National Physical Laboratory, and the calibration was used in the present calculations.

In order to minimise electrical leakage from the furnace heating spiral to he thermocouple and potentiometer, the cylindrical nickel liner contained in the furnace and separating the thermocouple from the porcelain furnace tube was earthed. In spite of this precaution a small leakage was still evident. The effect of this leakage was eliminated by placing a reversing switch in the furnace circuit and determining the balance point on the potentiometer wire for both directions of the furnace current. The difference in the balance point never exceeded 1° C.

Calculation of Results.

A series of ten curves was obtained for the purposes of calibration, the electrical energy supply varying from 0·28 to 0·42 watts. A series of five curves was obtained by admitting radiation from the furnace, the calculated energy supply varying from 0·28 to 0·34 watts.

The areas of the radiating and receiving apertures remained constant, while their distance apart and the temperature of the furnace varied from one experiment to another.

The results are embodied in the following table :—

Table I.

Area of furnace aperture = 2·800 cm.^{2}.
Area of receiving aperture = 1·070 cm.^{2}.

Temperature of furnace.	Distance between apertures.	Radiation received calculated from successive ordinates.					$\sigma \times 10^5$.
		5 mins.	8 mins.	10 mins.	12 mins.	Mean.	
°C.	cms.	watts.	watts.	watts.	watts.	watts.	erg/sec. cm.^{2} deg.^{4}.
1117	8·289	0·300	0·300	0·300	0·305	0·301	5·93
1115	8·289	0·296	0·297	0·297	0·297	0·297	5·86
1119	8·266	0·303	0·303	0·304	0·304	0·304	5·90
1120	8·266	0·305	0·305	0·305	0·305	0·305	5·90
1097	8·266	0·283	0·283	0·283	0·283	0·283	5·87

Mean value, $\sigma = 5·8(9) \times 10^{-5}$ erg/sec. cm.^{2} deg.^{4}.

Discussion of Results.

An objection to the present method of experiment lies in the fact that the energy to be measured and the energy used for the purposes of calibration are not introduced into the receiver in the same manner. An attempt to show that the objection is not serious was made by varying the position of the heating coil. If the cavity were a perfectly "black body," the resulting effect should be independent of this position. This point was tested in the following way: A separate heater, consisting of a single platinum wire, provided with the usual current and potential leads, was stretched across a diameter within the receiver. This position is very different from that of the original heating coil already described. A series of calibration curves was obtained, using this wire to carry the current, and the energy of the radiation streams from the furnace was calculated from these observations. The results differed by less than 1 per cent. from those obtained with the original heating coil. The small differences indicate that the energy losses

through the aperture are slightly greater when the diametric heating wire is used. Such an effect is to be expected, since this wire is stretched across the middle of the receiver, a position more favourable for direct radiation losses through the aperture. Owing to this fact, the calibration data obtained with the diametric heater were discarded.

It will be seen that the method of measuring the energy received is essentially the same as that used by Féry and Drecq,* but differs in two important respects. Firstly, the energy falls on a full receiver, and, secondly, the difficulty of temperature variation is avoided by using two such receivers differentially. Again, in Féry and Drecq's conical receiver the heating coil used for calibration was wound on the outer surface of the cone and was in contact with the liquid in the thermometer bulb. With a conical receiver the proportion of the calibrating energy retained will depend entirely upon the position of the heating coil, while in the present method there is evidence to show that this proportion is practically independent of the position of the coil. This fact makes it highly probable that equal quantities of energy put in as electrical energy and as radiation would produce the same effect.

Sources of Error.

In all previous determinations of the value of the radiation constant the receiver has not been a "black body." In some cases the arrangement of the screens has been such as to allow of additional energy reaching the receiver by radiation from the screens. The first point has already been discussed. With regard to the second it has been pointed out by a previous writer† that one of the most important screens in the arrangement of Féry and Drecq was not water cooled, and that it consisted of thick blackened cork containing a cylindrical hole, and from the surface of the cork additional energy would reach the receiving aperture by reflection. The additional energy received would make the resulting value of σ too high. In the arrangement described in the present paper (see fig. 4) additional radiation would reach the receiving aperture after undergoing two successive reflections. The screen facing the furnace would reflect some of the radiation it received from the furnace aperture to the screen facing the receiving aperture. This, again, would reflect to the receiving aperture. If the screens were not blacked, but left with a tarnished metal surface, reflecting, say, 50 per cent. of the incident energy, the writer calculated that σ would be 20 per cent. too high. This point was verified experimentally, the results of three such experiments being $\sigma = 7{\cdot}1, 7{\cdot}0$, and $7{\cdot}0 \times 10^{-5}$ erg/sec. cm.^{2} deg.^{4}.

* 'Journ. d. Phys.,' July, 1911, p. 558.

† Shakespear, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 180.

In all the experiments in Table I the screens were blacked. If it is assumed that the blackened surface used diffuses 5 per cent. of the energy it receives, then it may be shown by making similar approximations to those in the previous calculation that the value of σ would not be increased by more than 1 per cent.

Another source of error is due to the water-cooled cone of the furnace screen reflecting some radiation from the cooler part of the furnace into the receiving aperture. The calculation of the additional energy received by this means presents some difficulty, but a rough approximation shows that it is not more than 2 per cent. of the whole. The difficulty due to reflection from this cone may be overcome by reversing the furnace screen. This was impracticable in the present case, since the placing of the furnace farther back would diminish the pencil of radiation which must come from that region of the furnace in the neighbourhood of the thermocouple; and the apparatus was not capable of dealing with smaller quantities of energy with a very high degree of accuracy. For this and other reasons the screen was not reversed, but when the new high temperature full radiator is constructed, arrangements will be made to overcome the difficulty.

It may be pointed out that the error due to reflection from the cone will be compensated at least partially by that due to the furnace not being a full radiator.

The experiment has grown out of a suggestion made to me by Prof. J. H. Poynting, F.R.S., that in the measurement of σ it was desirable that both radiator and receiver should be full radiators; and to him and to Dr. Guy Barlow I wish to express my gratitude for their kindly interest throughout the work.

Appendix.

Calculation of the Energy Exchange between Two Fully Radiating Coaxial Circular Apertures at Different Temperatures.

For the following I am largely indebted to Mr. C. J. Lay.

The mutual illumination* of two such apertures of intrinsic brightness I may be written

$$\tfrac{1}{2}\mathrm{I}\iint \log r \cos\epsilon \, ds\, ds',$$

where ϵ is the angle between the tangents at ds, ds', and r is the distance between the elements ds, ds', of the boundaries. In this case put

$$ds = a d\theta \quad \text{and} \quad ds' = a\, d\theta',$$

then $$\cos\epsilon = \pm\cos(\theta-\theta'), \qquad r^2 = z^2+a^2+b^2-2ab\cos\epsilon.$$

* *Cf.* Hermann's 'Geometrical Optics,' p. 212.

For integration round the first circle put $\theta' = 0$. Then $\theta = \epsilon$ and we have

$$\tfrac{1}{4}\mathrm{I}a\iint \log(z^2+a^2+b^2-2ab\cos\theta)\cos\theta\,ds'\,d\theta.$$

Now $$\int_0^{2\pi}\log(\alpha-\beta\cos\theta)\cos\theta\,d\theta$$

$$= \Big[\sin\theta\log(\alpha-\beta\cos\theta)\Big]_0^{2\pi}-\beta\int_0^{2\pi}\{\sin^2\theta/(\alpha-\beta\cos\theta)\}\,d\theta$$

$$= -\beta\int_0^{2\pi}\{(\cos^2\theta-1)/(\beta\cos\theta-\alpha)\}\,d\theta$$

$$= -\beta\int_0^{2\pi}\left\{\frac{\cos\theta}{\beta}+\frac{\alpha}{\beta^2}+\left(\frac{\alpha}{\beta^2}-1\right)\Big/(\beta\cos\theta-\alpha)\right\}d\theta$$

$$= -2\frac{\pi\alpha}{\beta}+2\frac{\alpha^2-\beta^2}{\beta}\int_0^{\pi}\frac{d\theta}{\alpha-\beta\cos\theta}.$$

Now $$\int_0^{\pi}\frac{d\theta}{\alpha-\beta\cos\theta}=\frac{\pi}{\sqrt{(\alpha^2-\beta^2)}}.$$

Therefore we have

$$\tfrac{1}{4}\mathrm{I}a\left\{-2\pi\frac{\alpha}{\beta}+2\frac{\pi}{\beta}\sqrt{(\alpha^2-\beta^2)}\right\}$$

after the first integration, where

$$\alpha = z^2+a^2+b^2 \quad\text{and}\quad \beta = 2ab.$$

For the second integration the result must be the same whatever value of θ' we start with, hence we have only to replace ds' by $2\pi b$. We then get

$$\pi^2\frac{ab}{\beta}\{\sqrt{(\alpha^2-\beta^2)}-\alpha\}.$$

This gives the sign negative, which shows we ought to change the sign of $\cos\epsilon$; we then get

$$\tfrac{1}{2}\pi^2\mathrm{I}\{\alpha-\sqrt{(\alpha^2-\beta^2)}\} = \tfrac{1}{4}\pi^2\mathrm{I}\{2(z^2+a^2+b^2)-2\sqrt{[(z^2+a^2+b^2)^2-4a^2b^2]}\}$$
$$= \tfrac{1}{4}\pi^2\mathrm{I}(r_1-r_2)^2,$$

where $$r_1^2 = z^2+(a+b)^2, \qquad r_2^2 = z^2+(a-b)^2.$$

Since $\mathrm{I} = \mathrm{R}/\pi$, we have

$$\mathrm{E} = \tfrac{1}{4}\pi\mathrm{R}/(r_1-r_2)^2.$$

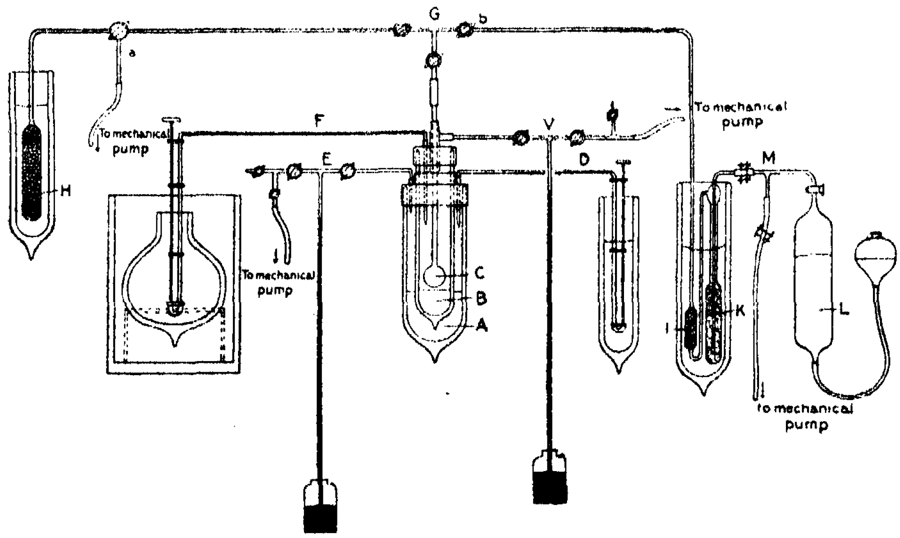
Optical Investigation of Solidified Gases. II.—The Crystallographic Properties of Hydrogen and Oxygen.

By Walter Wahl, Ph.D.

(Communicated by Sir James Dewar, F.R.S. Received September 19,—Read November 21, 1912.)

In a recently published paper I have described a method and apparatus for the optical investigation of crystalline nitrogen and argon and other bodies solidifying at extremely low temperatures.* The determination of the general crystallographic characters of these bodies by crystal-optical methods was also described.

The following communication deals with the optical investigation of solid hydrogen and oxygen. In order to liquefy and solidify hydrogen in the crystallisation vessel described in the paper mentioned it is necessary to use liquid and solid hydrogen as cooling agents, and the apparatus for the investigation of nitrogen and argon has accordingly had to be modified. Fig. 1 shows the arrangement of the apparatus used for working with liquid hydrogen.



A is a silvered vacuum vessel provided with two observation slits. Through a metal cap a long, narrow, test-tube shaped vacuum vessel, B, is fixed into the vacuum vessel A. Through the same cap a syphon, D, by which liquid

* 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 371.

air can be admitted, and a tube connected with the mechanical pump and the mercury barometer-valve, E, are inserted. The inner vacuum vessel, B, is also fitted with a metal cap provided with a T-piece tube through which the stem of the quartz-glass crystallisation vessel, C, leads. Through another tube in this metal cap is inserted a syphon, F, by which liquid hydrogen can be admitted. The vertical part of the T-piece tube is, as far up as the branch tube in the centre of the cap, wider than the quartz-glass stem of the crystallisation vessel. This branch tube is connected with a mercury barometer valve, V, and also to the mechanical pump, so that the liquid hydrogen in the inner vacuum vessel can be exhausted. The stem of the quartz-glass crystallisation vessel is connected to a T-piece, G, of glass, fitted with three stopcocks, by means of a short piece of rubber pressure tubing. The one branch of the T-piece G is sealed on to a three-way stopcock, a, and a large charcoal bulb, H. The other branch is sealed on to a U-tube, I, containing a few grammes of charcoal, and to this is connected a narrow glass vessel, K, of the wash-bottle type, containing asbestos wool. K is, in turn, connected to a small mercury gasometer, L, containing pure hydrogen. A T-piece, M, the branch tube of which is connected to a vacuum pump, is inserted between the vessel K and the gasometer L. The connecting rubber tubes of this T-piece can be closed by two screw-clamps, so that the gasometer can, if necessary, be detached from the apparatus during the course of the investigations in order to fill it with more hydrogen.

Two more charcoal bulbs, each connected with the interior of one of the vacuum vessels surrounding the crystallisation vessel, were employed in order to dry the glass surfaces before the liquid air and liquid hydrogen were admitted through the syphons, D and F. Afterwards, however, it was discovered that the moisture from the glass walls would condense into the liquid air on the bottom of the vessel and could be frozen out on the glass walls of the lower part of the vessel if only a few drops of liquid air were admitted through the syphon to begin with.

As in these experiments with hydrogen and oxygen the cooling liquids were not allowed to cover the crystallisation vessel it was not necessary for them to be absolutely clear, and the two charcoal bulbs were therefore omitted in order to render the apparatus more simple.

Before the apparatus was cooled, the charcoal bulbs H and I, as well as the asbestos vessel K, were thoroughly heated and exhausted through the three-way stopcock, a. This three-way stopcock was then turned so that the charcoal in H remained in communication only with the interior of the crystallisation vessel and the tubes, I and K, containing charcoal and asbestos.

The charcoal bulb, H, was now immersed in liquid air and in this way the crystallisation vessel and the tubes connected with it were thoroughly exhausted. After the charcoal bulb had been turned off, hydrogen was admitted from the gasometer to the crystallisation vessel, and this latter again exhausted by the charcoal exhaust. The crystallisation vessel and the tubes connected with it were in this way washed out with hydrogen several times by alternately admitting from the gasometer and exhausting. The tubes I and K, containing charcoal and asbestos, were then immersed in liquid air and the charcoal in I saturated with hydrogen from the gasometer.

Liquid air was then admitted to the outer vacuum vessel through the syphon D—at first only a few drops, as described above, but later sufficient to cover the lower part of the inner vacuum vessel. After the liquid air in the outer vacuum vessel had been kept under exhaust for some time liquid hydrogen was admitted to the inner vacuum vessel through the syphon F, and was only allowed to cover the lower part of the crystallisation vessel. By exhaustion with the mechanical pump, the liquid hydrogen in B could easily be cooled down sufficiently for it to crystallise.

Hydrogen.

Pure hydrogen is admitted to the crystallisation vessel from the gasometer, and is freed from any possible trace of moisture, hydrocarbons, or other impurities, by passing it through the tubes containing asbestos wool, K, and cocoanut charcoal, I, immersed in liquid air.

The hydrogen is then caused to liquefy in the crystallisation vessel by cooling this in the vapour of the hydrogen contained in the inner vacuum vessel, and which is in a state of evaporation due to reduced pressure. When a sufficient quantity of liquid hydrogen is condensed in the crystallisation vessel, the stopcock *b* of the T-piece G is closed, and the liquid hydrogen cooled down as much as possible by exhausting the surrounding solid hydrogen in the inner vacuum vessel B.

The crystallisation of the hydrogen is then easily effected by placing the crystallisation vessel in communication with the charcoal bulb H. In such circumstances crystallisation takes place almost instantly and a fine-grained crystalline mass is formed. The crystals rapidly melt again when the charcoal exhaust is disconnected. If liquid hydrogen is now admitted in small quantities through the syphon, while the hydrogen in the inner vacuum vessel is kept solid by exhaustion, each splash of hydrogen is instantly solidified and causes, when it strikes the outer walls of the crystallisation vessel, part of the liquid hydrogen in this to crystallise.

Under such conditions crystal growth-structures are formed, but melt

again almost instantly. Crystallisation takes place from one or more nuclei and crystal needles grow, with extreme velocity, in all directions, forming a cluster of radiating needles very similar in appearance to the well known "tourmaline suns," as found, for example, in Cornish granite. Sometimes one or more of these needles grow much longer than the others and are more hair-like and occasionally bent.

These experiments show that the velocity of the crystallisation of hydrogen is extremely great, in spite of the fact that crystallisation takes place at such a low temperature, only about 20° above absolute zero.

Both the fine-grained crystal mass obtained by charcoal exhaust, and the needle-shaped parts of the growth-structures are absolutely isotropic. As these needle-shaped parts of the growth-structures cannot form part of a hexagonal or tetragonal crystal growth-structure parallel to the basal plane of the crystal, we are justified in concluding that hydrogen crystallises in the regular system. The needle-shaped branches of crystal growth-structures usually grow at right angles to a crystal face of the fully developed crystal, and we may therefore conclude from the formation of bundles of crystal needles, radiating from one centre in a great number of directions, that the hydrogen crystals, when fully developed, belong to one of the forms of the regular system rich in crystal faces, *i.e.*, the trisoctahedron or the hexoctahedron.

Oxygen.

Pure oxygen was prepared by heating potassium permanganate which had previously been dried in a charcoal vacuum. The gasometer containing the oxygen over mercury was connected directly to the T-piece G, fig. 1, leading to the crystallisation vessel, the tubes I and K, filled with charcoal and asbestos, not being necessary in this case.

When the apparatus had been exhausted and washed out with oxygen, liquid air was admitted to the outer vacuum vessel and liquid hydrogen to the inner one. This was done as previously described in the case of hydrogen. The stopcock *b*, of the T-piece G, was then opened, and oxygen from the gasometer liquefied in the crystallisation vessel. The liquid oxygen easily solidified when cooled in the vapour of the liquid hydrogen. In order to again liquefy the crystallised oxygen it was necessary to wait until most of the liquid hydrogen had evaporated from the inner vacuum vessel, which, on account of the good heat isolation at the bottom of the inner vessel, takes some considerable time. In consequence it was not possible to make as many observations as would otherwise have been possible with the quantity of liquid hydrogen available.

The solidification of oxygen was found to be a somewhat complicated phenomenon, but of much interest. When the liquid is cooled it becomes viscous before crystallisation sets in. The crystals which are formed in this apparently stiffened mass are not well developed, and grow very slowly. If the cooling takes place rapidly these crystals cease to grow altogether, the liquid probably becoming too viscous to permit any further growth. The product obtained is, in such circumstances, a stiffened mass of liquid oxygen, with oxygen crystals embedded in it. In order to obtain a homogeneous crystallised product the cooling must take place very slowly, which is not easy when a very small piece of apparatus, as the crystallisation vessel in this case, is cooled by a spray of liquid hydrogen from the syphon.

Liquid oxygen, on cooling, thus behaves in a manner analogous to most silicates and borates, which, when rapidly cooled, give a glass with varying quantities of crystals embedded in it. The crystals of oxygen are dark between crossed nicol prisms, similar to the surrounding stiffened liquid.

When the oxygen in the crystallisation vessel is cooled further by liquid hydrogen vapour, a transformation of the whole mass into a fine grained crystal mass takes place almost instantaneously. These crystal grains are strongly double refracting. Oxygen is thus polymorphous. The crystal grains resulting from the transition into this second modification are, however, so small and of such irregular shape that it was not possible to determine to what crystal system they belong.

During the experiments carried out so far, the liquid oxygen was not cooled sufficiently quickly to produce a homogeneous stiffened mass without any crystals of form I being embedded in it, and it is uncertain whether such a homogeneous oxygen glass could be obtained at all by rapid cooling. It is possible, however, that the oxygen glass, if once produced without containing any crystals of form I, would remain as a glass at still lower temperatures, and the crystal modification II not be formed at all in the absence of crystals I. Or, the supercooled oxygen might at a low temperature crystallise ("devitrify") directly as form II, just as liquid sulphur, when supercooled in certain circumstances, may crystallise directly as rhombic sulphur.

It is probable, however, that when both crystals of form I and residual parts of liquid are present simultaneously, the transition at first takes place in the crystal phase, and that as soon as the crystals II are formed in the crystals I they act as germs, and a kind of devitrification of the remaining stiffened liquid into form II takes place simultaneously with the transition in the crystalline phase. On account of the rapidity with which the whole

process of formation of this double refracting mass of crystals takes place, it was not possible to observe directly how the devitrification of the non-crystalline parts into form II actually took place.

Under the conditions in which these experiments were conducted a rapid transition into the fine grained modification II always took place at low temperatures. When, however, the temperature was lowered as much as possible by exhausting the solid hydrogen, which reached just up to the lower part of the crystallisation vessel, no further alteration of the product of this first transition could be observed.

The above refers to observations on oxygen at diminishing temperatures. At increasing temperatures it is easier to investigate both the transition from one form into the other and also the properties of form I. This depends partly upon the fact that it is not so easy to lower the temperature of the crystallisation vessel gradually and evenly, by admitting liquid hydrogen through the syphon into the vacuum vessel B, as it is to increase the temperature very slowly by letting the surface of the liquid hydrogen sink gradually by evaporation, and partly because it is easier to study the properties of form I, when it is obtained by transition from form II, than when it is obtained by the crystallisation of the stiffened liquid.

In the apparatus shown in fig. 1 the isolation of the crystallisation vessel is extremely good, and the liquid hydrogen at the bottom of the vacuum vessel B only evaporates very slowly. When evaporation has gone on for some time a very marked vertical temperature gradient is formed above the surface of the liquid hydrogen. Consequently the temperature in the crystallisation vessel rises very slowly, and a certain temperature will first reign in the upper part and then gradually move downwards as the surface of the liquid hydrogen sinks in the vacuum vessel. Any definite temperature, as for instance that of the transition point or that of the melting point, passes therefore from the upper part of the crystallisation vessel slowly downwards. The transition and the melting will thus occur along each of two horizontal lines which move slowly downwards. If, as in this case, the two temperatures are not far apart, it is possible to see the two border lines simultaneously in the crystallisation vessel.

The border line between the second and first crystalline modifications is easily visible to the naked eye as a sharp line below which the preparation looks white and nearly opaque on account of its finely granular structure. The modification I is quite clear and translucent, so that it is not so easy to observe the border line between it and the liquid with the naked eye, although it is easily visible under the microscope. In the parts of the crystallisation vessel above the crystals I, where a temperature reigns only slightly above

that of the melting point, the liquid appeared stiff. Higher up, however, in the stem of the vessel it was quite fluid, while the border line crystals I—crystals II was still in the lower part of the vessel.

The crystal field I, lying between the two horizontal border lines, appears in most cases quite homogeneous and is dark between crossed nicols. Near the border line crystals—liquid, however, where the temperature approaches that of the melting point, it can be seen that it really consists of a great number of crystal grains, quite uniform in size and of hexagonal shape. Only in two instances did the crystal field appear differently: It consisted of long flat prismatic crystals standing at right angles to the border lines and growing at the lower end on the expanse of the strongly double refracting grains of modification II. These prisms had no even border line between each other but were otherwise well developed. The extinction is parallel to the prism axis, and the double refraction low, of about the same magnitude as that of ordinary quartz in sections parallel to the axis.

From these observations at rising temperatures the crystal modification I must be considered hexagonal. On crystallisation from the liquid the crystals always grow parallel to the basal plane, and appear dark between crossed nicols, just as ordinary hexagonal ice, for example, always crystallises with the basal plane parallel to the water surface. Again, when the modification I is formed by transition from form II, it also, in most cases, grows with the basal plane parallel to the glass surfaces, and appears dark between crossed nicols. In two instances, however, the growth described above occurred at right angles to the glass surfaces.

The width of the double vacuum vessels unfortunately does not permit of an investigation in convergent polarised light. The form of the crystal grains, however, which, as mentioned, becomes visible near the border line crystals—liquid by a kind of "etching" on melting, confirms the conclusions drawn from the observations in parallel polarised light, that the crystals I are hexagonal.

The exact temperature of the transition point crystals I to crystals II has yet to be determined, but, from the fact that the two horizontal border lines between crystals II and crystals I, and crystals I and liquid, observed during the experiments at rising temperatures, lie so close to each other, we may conclude that the transition point temperature is not far below the melting point temperature.

The melting point of oxygen has been given by Estreicher* as -227°. Quite recently Sir James Dewar and Prof. Kammerlingh-Onnes have, independently of each other, determined the melting point temperature†

* T. Estreicher, 'Bull. Intern. de l'Acad. des Sciences de Cracovie,' 1903, p. 836.

† Dewar, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 597.

and found a much higher temperature: $-219°$ and $-218{\cdot}4°$. It appears not improbable that the temperature determined by Estreicher has been that of the transition point crystals I to crystals II and not at all that of the melting point. Estreicher observed a halt in the rising of the helium thermometer and noticed also that the upper part of the oxygen in his vessel at the same time appeared clear and "molten." In a vessel like the one employed by Estreicher, the crystals II must have appeared quite white and opaque like a snowy mass, and, as the crystals I will form a comparatively translucent mass above this, the transition point might easily have been taken for the melting point, and the true melting point overlooked. This is the more probable as Estreicher employed a single vacuum vessel which was closed only by a wad of wool, and the inner vessel containing the oxygen therefore could not have been very easy to observe.

Another indication that the transition point temperature is close to the melting point temperature is supplied by the observation of Sir James Dewar,* that—"Under the continued exhaust of the charcoal the smooth surface† of the oxygen became gradually broken up by numerous cracks penetrating but slowly down into the mass, and giving it the appearance of having a white, crystalline surface.‡ This disappeared very rapidly on turning off the charcoal exhaust, and the surface became quite smooth, although, with the good isolation, no appreciable melting could be detected for 15 minutes or more." These observations quoted from the paper of Sir James Dewar seem to indicate that the transition point temperature crystals I—crystals II can be reached by continued charcoal exhaustion on the solid oxygen, whereby the surface of the oxygen mass thus transformed into the crystalline form II becomes cracked and of a white appearance. In four different series of experiments the pressure, when the charcoal vacuum was turned off, is given by Sir James Dewar as 0·467, 0·43, 0·4280, and 0·465 mm., rising rapidly and then remaining constant at about 1·11 to 1·12 mm. for some thirty minutes during melting. The exhaustion had in all cases been carried to about 0·3 mm., and the constancy of the value obtained immediately after the charcoal vacuum had been disconnected indicates that this value 0·46 mm. is the triple-point-pressure crystals I—crystals II—vapour. The pressure then rises rapidly to 1·12 mm., which must be regarded as the triple-point-pressure crystals I—liquid—vapour.

Most of the physical constants of solid oxygen are determined at the boiling point of hydrogen, and they must therefore be regarded as the constants of the second crystalline modification of oxygen. The observations on the crystallisation and melting of oxygen described above indicate that

* Dewar, *loc. cit.*, p. 594. † Crystals I (?). ‡ Crystals II (?).

in order to determine any constants of modification I, it would be necessary preliminarily to cool the oxygen below the transition point temperature, and then investigate the product obtained by transition from form II, as a mixture of super-cooled, stiffened liquid containing varying quantities of crystals—depending on the conditions of cooling—may be arrived at by crystallising the oxygen directly from the liquid state. The cracking up of the mass during transition to form II, and the opaqueness of the product, indicate a not inconsiderable change of volume, the modification II being the denser one. The same phenomena, however, will render it difficult to obtain correct values of the density of this modification of solid oxygen when contained in a closed and rigid vessel.

The latent heat of transition of the one form into the other is probably considerable, as Estreicher states that he observed a distinct halt in the rise of his helium thermometer, at what is here considered to be the transition point.

The existence of two crystalline modifications of oxygen is interesting with regard to the position of oxygen in the periodic classification of the elements, and the analogy existing between the compounds of oxygen and sulphur. By the discovery of similar polymorphous relations, this analogy is now extended to the elements themselves.

The investigations have been executed in the Davy-Faraday Research Laboratory of the Royal Institution. I am indebted to Prof. Sir James Dewar for kind advice regarding these determinations at liquid hydrogen temperatures, and for placing at my disposal the vacuum vessels, syphons, and the necessary quantities of liquid air and of liquid hydrogen. I also wish to thank Mr. W. Green, B.Sc., of the Davy-Faraday Laboratory, for valuable help during the experiments.

The Photo-electric Behaviour of Iron in the Active and Passive State.

By H. STANLEY ALLEN, M.A., D.Sc., Senior Lecturer in Physics at University of London, King's College.

(Communicated by Prof. C. G. Barkla, F.R.S. Received October 17,—Read December 5, 1912.)

The discoveries of Hertz and of Hallwachs showed that a polished metal plate exposed to ultra-violet light readily loses a negative electric charge, but retains a positive charge. If an electric field is applied by making the metal form one plate of an air condenser, whose second plate is charged positively by a battery, the saturation current obtained may be regarded as a measure of the photo-electric activity of the metal.

It has been known for more than a century that ordinary iron, which is acted on energetically by dilute nitric acid, can be made to assume a passive condition by immersion in strong nitric acid. The same condition can be produced by other powerful oxidising agents, or by using iron as the positive electrode in an electrolyte containing oxygen. The nature of the change that takes place when iron passes from the active to the passive state has given rise to much discussion, but none of the explanations suggested has yet met with general acceptance.*

The experiments to be described were carried out in order to compare the photo-electric activity of iron in the active state with that of the same sample in the passive state. It was hoped that the results might throw some fresh light on the theory of "passivity." The experiments prove that iron which is chemically active is active in the photo-electric sense, while iron which is passive shows much smaller photo-electric activity, in some cases none that can be detected. The bearing of these results on the nature of "passivity" will be discussed later.

Measurements of the Photo-electric Activity.†

The photo-electric activity of the plate under test was measured by determining the rate of leak between the plate and a parallel gauze of iron wire charged to 100 volts. The current was found by observing the

* Useful summaries of the literature of "passivity" have been published by Heathcote ('Soc. Chem. Ind. Journ.,' 1907, vol. 26, pp. 899—917) and Byers ('Amer. Chem. Soc. Journ.,' 1908, vol. 30, pp. 1718—1742).

† I am indebted to the Government Grant Committee of the Royal Society for some of the apparatus used in this research.

rate of movement of the needle of a Dolezalek electrometer with one set of quadrants in connection with the plate. A mercury vapour lamp of fused quartz by Heraeus was used to illuminate the plate through the meshes of the gauze. Before commencing a series of observations the lamp was allowed to burn at least 20 minutes so that it might assume a steady state. In this paper the photo-electric activity of the iron plate is expressed in terms of the activity (arbitrarily assumed as 100 units) of a standard plate of pure silver supplied by Messrs. Johnson, Matthey and Co. Previous experiments by the author* proved that this silver plate showed no photo-electric fatigue when kept in an air-tight brass testing vessel.†

The iron plates used in these experiments were cut from Kahlbaum's sheet iron, 0·2 mm. thick. They were in the form of circular discs 5·1 cm. in diameter, a projecting piece 2 cm. long and 1 cm. wide being left at one part of the rim to serve as a handle. In some cases smaller plates (3 cm. in diameter) of the same shape were used. Rods of commercial iron and steel were also examined. The rods, which were 5 cm. long and 0·6 cm. in diameter were polished in the lathe with fine emery paper. As all the tests for photo-electric activity had to be made with a dry plate, it was necessary, after having rendered the iron passive, to dry it without destroying the passivity The method followed was that recommended by Heathcote. The passive iron was washed by the following solutions in turn:—

1. Saturated aqueous solution of potassium bichromate + 2·8 grm. potassium hydrate per 100 c.c. solution of bichromate.
2. Water 100 c.c., pure methylated spirits 10 c.c., potassium hydrate (by alcohol) 2·5 grm.
3. Absolute alcohol.

The solutions were sprayed or poured on to the plate as quickly as possible one after the other. The manipulation was easier for the rods than for the plates, and easier for the small plates than for the large ones.

In Heathcote's experiments the following test was employed in order to determine whether the iron plate was in the active or in the passive state:—

"The rod was regarded as passive when, after plunging in 1·2 nitric acid and shaking for a moment in the acid and then holding motionless, no chemical action could be detected at the surface by the unaided eye, the temperature of the acid being about 15°—17° C."

In the present experiments little difficulty was found in applying this test in the case of wires, small plates or rods. A passive wire or small plate could be kept in this dilute acid for some time without chemical action, but

* 'Phil. Mag.,' 1910, vol. 20, p. 570.

† 'Roy. Soc. Proc.,' 1907, A, vol. 78, p. 484.

with the larger plates chemical action generally set in after the iron had been immersed for 15 or 30 seconds. A single spot of active iron is sufficient to start the reaction, and the difficulty experienced with the larger plates is probably due to the extent of the sharp edge forming the circular boundary of the plate.

Summary of Experimental Results.

The experiments in which plates of Kahlbaum's iron were rendered passive by immersion in strong nitric acid (specific gravity, 1·5) proved that such treatment reduced the photo-electric activity to considerably less than one-half of the value for the active plate, and that when reduction was most marked the plate was most distinctly passive.

The following extracts from the laboratory note-book illustrate the results:—

	Photo-electric activity.
PLATE F, diameter 5·1 cm.:—	
Plate cleaned with nitric acid and water, washed under tap, and then with solutions 2 and 3	144
Plate begins to dissolve at once in dilute nitric. Transferred to strong nitric, where action soon stops. Wash with solutions 1, 2, and 3	11
Plate tested in dilute nitric, is passive for 30 secs. Wash under tap and then with solutions 2 and 3	70
Another experiment. Initial activity of plate	98
Dry iron plate, immersed in strong nitric, then washed with solutions 1, 2, and 3	13
Plate tested in dilute nitric, remains passive about 5 or 10 secs. Washed under tap, and while *wet* placed in strong acid. Wash with solutions 1, 2, and 3	18
Plate remains passive for 10 secs. in dilute acid. Wash under tap and then with solutions 2 and 3	147

Results of a similar character were obtained with the rods of commercial iron and steel. The photo-electric activity, measured after treatment with strong nitric acid, was extremely small, and in some cases too small to be detected.

Experiments were also carried out in order to compare the behaviour of iron after being used as anode, and after being used as cathode, in a voltameter containing dilute sulphuric acid. According to Heathcote (*loc. cit.*): "The current density must be above a certain value for passivity to ensue. Iron behaves as if one could teach it to become passive; repeated trials end in success, and, once passivity has been produced, its reproduction is facilitated." "If the anode be sprayed with alkaline potassium bichromate solution as it is withdrawn from the sulphuric acid, it can be dried and kept 15 hours in a laboratory atmosphere without becoming active to 1·2 nitric acid."

By using small plates of Kahlbaum's iron, I have been able to show that photo-electric activity after use as anode is extremely small, but the experiments with the larger plates were not successful. In consequence of the difficulties in manipulating these plates, the later experiments were carried out with cylindrical rods of iron and steel. The rod formed one electrode, and was surrounded by a cylinder of thin sheet iron, which constituted the second electrode. In this way all parts of the rod were acted upon similarly. The rod was mounted so that it could be lifted vertically out of the voltameter, and washed with the solutions, without any risk of its coming into contact with the second electrode. The current was supplied by four secondary cells, giving 8 volts, and an ammeter and adjustable resistance were included in the circuit.

IRON ROD:—	Photo-electric activity.
Initial activity	60
Iron rod made cathode for 1 min., current 0·5 ampère, then washed with solutions 2 and 3	80
Iron rod made anode for 1 min., current 0·5 ampère, then washed with solutions 1, 2, and 3	Less than 4
Iron rod made cathode for 1 min., current 0·5 ampère, then washed with solutions 2 and 3	70
Iron rod made anode for 1 min., current 1·0 ampère, then washed with solutions 1, 2, and 3	Less than 2
Rod immersed in dilute nitric, not visibly acted upon at the moment of immersion, but action quickly begins.	

A steel rod gave similar results.

Discussion of Results.

The results just recorded may be summarised by saying that processes which render iron active in the chemical sense give it large photo-electric activity, while processes which render iron passive tend to greatly diminish the photo-electric activity, in general to less than half the value observed with an active plate. It must be borne in mind that in these experiments the photo-electric activity is measured with a dry plate, while the chemical activity is tested in solution, and that the processes employed in changing the state of the iron are all wet processes. We may extend our conclusions by including the observations of Muthmann and Frauenberger,* who state that "metals become passive on lying in the air, and their potentials (in KCl solution) assume medium values, whilst vigorous mechanical cleaning of the surface renders them active." Here the reference is to chemical activity, but the statement is equally true if interpreted of photo-electric activity.

* 'Zeit. Elektrochem.,' 1904, vol. 10, pp. 929, 930.

Metals exposed to the air show photo-electric fatigue, whilst polishing the surface gives rise to a large photo-electric current.

We appear to be justified in assuming a correlation between these two sets of phenomena and in saying that the chemical activity and the photo-electric activity vary together. If this view be correct we see that there are degrees of activity and also of passivity, a conclusion which appears to be in accordance with the general experience of chemists. Further, we may regard the photo-electric fatigue sometimes observed with iron as a gradual passage from the active to the passive state. The experiments of the author* and others support the conclusion of Hallwachs that the principal cause of fatigue is to be found in the condition of the layer of gas at the surface of the plate. We should, therefore, be inclined to attribute passivity to the surface film of gas. The fact that from the photo-electric standpoint different degrees of activity can be obtained from the same iron plate does not harmonise well with the idea of an allotropic change as the cause of chemical passivity; it agrees far better with the idea of a protective coating, whether of oxide or of gas, and best of all with the last named, *i.e.* a gaseous film.

It must, of course, be admitted that such an explanation, whether applied to passivity or to photo-electric fatigue, cannot be regarded as final or complete until we are able to describe with greater definiteness the character of the modification in the gaseous layer to which the effects are attributed.

Conclusion.

1. The investigation into the photo-electric behaviour of dry iron shows that when the iron is chemically active it exhibits large photo-electric activity, while in the passive state this activity is greatly diminished.

2. It is held that this result is in good agreement with the theory which attributes passivity to the condition of the gaseous layer at the surface of the metal.

* 'Brit. Assoc. Rep.,' 1910; 'Phil. Mag.,' 1910, vol. 20, p. 572.

The Penetrating Power of the γ-Rays from Radium C.

By Alexander S. Russell, M.A., Carnegie Research Fellow of the University of Glasgow.

(Communicated by Prof. E. Rutherford, F.R.S. Received November 14,—Read December 5, 1912.)

The primary object of the present research was to find out if there is any residual radiation from radium C after the γ-rays of ordinary penetrating power have been entirely absorbed. In the course of the work it was necessary to measure the absorption of the γ-rays by mercury. This, also, has therefore been investigated in some detail. Only experimental results are given in this paper. A discussion of the theoretical meaning of the results will be given in a subsequent paper dealing with hardening and scattering of γ-rays.

A very penetrating radiation may be looked upon either as a new type of radiation, resembling the γ-ray in that it is uncharged, but possessing a much greater penetrating power, or, if the assumption be made that the γ-rays are heterogeneous, as the most penetrating constituents of the γ-ray beam. The recent work of Danysz* has shown clearly that some of the β-rays from radium C are ejected with a velocity not less than 99 per cent. of that of light. It is not unreasonable to expect that there are γ-rays corresponding to these, and possessing, therefore, a much greater penetrating power than the average penetrating power of ordinary γ-rays. This radiation, if it exists, would be present in the γ-ray beam only in very small amount, and detectable, therefore, only when a large source of radium is used, and special precautions taken.

In a previous paper it has been shown by F. and W. M. Soddy and the author† that, when measured under conditions such that no scattered radiation of any kind enters the electroscope, the γ-rays are absorbed, apparently according to a strictly exponential law, over a range of thickness of lead of 2 to 22 cm.; or, expressed mathematically, if I_{t_1} be the intensity of the γ-rays after traversing a thickness t_1 of metal, I_{t_2} the intensity after traversing a thickness t_2, it was found experimentally that

$$I_{t_2}/I_{t_1} = e^{-\mu(t_2-t_1)},$$

where e is the base of the natural system of logarithms, and μ is a constant,

* J. Danysz, 'Compt. Rend.,' 1911, vol. 153, pp. 339, 1066; 'Le Radium,' 1912, vol. 9, p. 1.

† F. and W. M. Soddy and A. S. Russell, 'Phil. Mag.,' 1910, vol. 19, p. 725.

the absorption coefficient. μ is constant from 2 to 22 cm. of lead, and has the value 0·498 cm.$^{-1}$.

In this work, difficulty was experienced in making accurate measurements from the 18th to the 22nd cm., owing to the smallness of the ionisation from the source of radium used. For this reason, it was impossible to say with certainty, whether or not there was any radiation which penetrated the greater of these thicknesses. The result found indicated that the effect due to these rays, if it exists at all, must be very small. It was desirable therefore to repeat the work under more favourable conditions with a large quantity of radium C. To detect this very penetrating radiation, the following conditions were thought most likely to give the desired result:—

(1) A strong source of radium C to be placed as near the detecting vessel as possible. This requires the use of as dense a metal as possible as an absorbent of ordinary γ-rays.

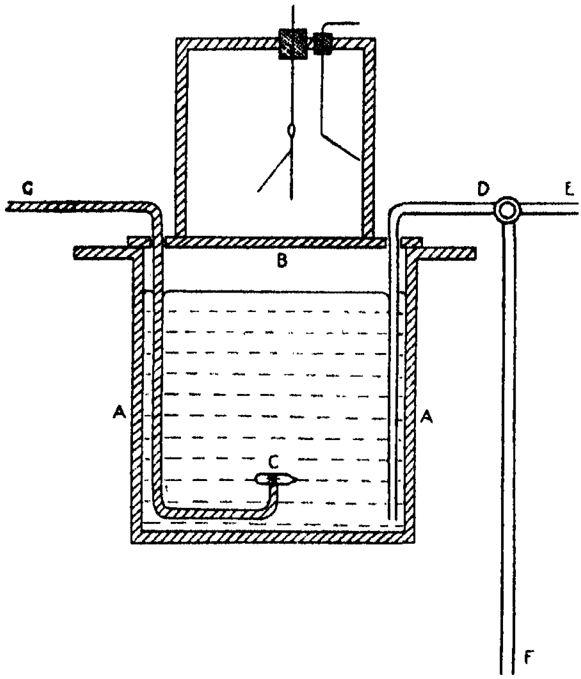
(2) Total exclusion of any scattered radiation from entering the electroscope through the sides and top.

(3) A detecting vessel which is sensitive and possesses a very low natural leak. It is essential that the ionisation chamber be large, in order that the air it contains may have a good opportunity of being ionised by the rays.

The reasons for these conditions are sufficiently obvious, and need not be discussed at length. The source used at the commencement of the experiments was about 300 millicuries of emanation. Mercury was employed as absorber of the γ-rays, as it has a greater density than any other common metal; and, therefore, a given thickness of this metal absorbs more γ-rays than the same thickness, say, of lead. The effect of scattered radiation was obviated by surrounding the source of rays on every side by at least 10 cm. of mercury. This reduced the rays moving in every direction to a very small percentage of their original intensity. Any scattered radiation, produced by the rays which escaped, was completely absorbed by the thick lead walls of the electroscope.

On p. 77 is given a diagram of the apparatus used in the chief experiment. A is a cylindrical pot of cast iron, of inside diameter 30·5 cm., and inside height 33·5 cm. When filled to the top it held 350 kgrm. of mercury. On top of this pot was laid a circular disc of lead B, 35 cm. in diameter, and 1 cm. in thickness. A large electroscope of the ordinary type was placed on the disc. The lead used for the disc and for the electroscope was the oldest procurable, in order that the latter might have as low a natural leak as possible. The electroscope had an inside diameter of 20 cm., an inside height of 21·5 cm., and a wall thickness of sides and top of 1 cm. It contained 6·75 litres of air. The leaf system consisted of a strip of brass,

7 cm. long, to which was attached a gold leaf, 6 cm. long. Insulation was effected by means of a very small bead of sulphur. Two cylinders of lead, 6 cm. long and 3 cm. inside diameter, and 1 cm. wall thickness, encircled the windows to prevent any scattered radiation from entering through them. The windows were circular and of the same diameter as the lead cylinders. The latter were just large enough to allow the reading microscope to be inserted. The microscope used had a magnification of about 9·5.



The source of radium emanation was contained in two sealed glass tubes, C, which could be attached by means of string to one end of an iron rod. The rod was connected by a clamp at G to a stand, and bent in such a way that, by raising or lowering G, the radium could be raised or lowered centrally in the mercury. By means of the glass apparatus D, which contained a three-way tap, the mercury could be added to the pot by pouring it in through E, or withdrawn by siphoning it off through F. The pot was carefully made and had a very uniform diameter. From the weight added to or withdrawn from the pot, therefore, the increase or decrease of thickness of the mercury covering the radium could be easily calculated. The natural leak of the electroscope was 0·45 division per minute, which was considered low for an instrument of these dimensions. One millicurie of emanation at a distance of 25 cm. below the lead base of the electroscope gave a leak of 36 divisions per minute.

Attempts to Detect the very Penetrating Radiation.

Two different experiments were made to detect the very penetrating radiation. The first was done at atmospheric pressure with the apparatus described above, the second was done with an ionisation chamber at high pressure. The first experiment was carried out as follows: The pot was filled to the top with mercury, and the natural leak measured three times for intervals of about 40 minutes each, with the source of radium removed entirely from the laboratory. The radium was then inserted to a depth of 20 cm. below the mercury, and the leak measured over a period of 20 minutes. The value of the leak obtained was considerably higher than the natural leak. The radium was then lowered to various depths, the leaks being carefully measured at each position, until a depth was reached at which there was no difference between the leak measured and the natural leak. The results actually obtained are given in the accompanying table:—

Table I.

Depth of radium below the mercury in cm.	Leak in division per min.
20	1·44
22	0·64
25	0·48
27	0·45
30	0·44
33	0·45

Natural leak, 0·45, 0·46, 0·44 division per min.

It is seen that at a depth of 25 cm. the ionisation due to the γ-radiation is only 7 per cent. of the natural leak of the electroscope. At greater depths this leak disappears entirely. There is, therefore, no γ-radiation capable of penetrating 27 cm. of mercury and of being detected in the electroscope used. The experiment shows also the complete absence of any secondary radiation entering the electroscope otherwise than through the base.

An ionisation chamber capable of withstanding a pressure of 80 atmospheres, was next used instead of the electroscope as a detecting vessel. The apparatus was kindly placed at my disposal by Mr. D. C. H. Florance, who employed it in a research which will soon be published. Inside the pressure chamber were mounted centrally two concentric cylinders of brass. The outer one was 22·5 cm. long and 6·3 cm. in diameter, the inner one 21·6 cm. long and 1·9 cm. in diameter. The former was charged to a

potential of 1500 volts, the latter was connected to one pair of quadrants of a sensitive Dolezalek electrometer. The pressure chamber itself was earthed.

Ionisation took place in the space between the cylinders. The pressure in the chamber was kept constant at 80 atmospheres. This arrangement is not so sensitive as the large electroscope, but it was used for two reasons. It is possible that the very penetrating rays might ionise dense gases only. Secondly, a large quantity of incident and emergent β-radiation from the very penetrating γ-rays might be produced when they strike the brass cylinders. Such radiation when produced would be an efficient ioniser of a gas at high pressure. When the radium was sunk to a depth of 26 cm. in the mercury, however, the leak of the electrometer was exactly the natural leak. No trace whatever of any radiation could be detected. I have to thank Mr. Florance for kindly making the necessary measurements for me.

The Absorption of the γ-Rays by Mercury.

The absorption of the γ-rays of radium C by mercury over a range of thickness of 1–22·5 cm. was next investigated. The radium was inserted centrally below the electroscope at a distance of 25 cm. and the pot filled with mercury. The leak was then measured. Ten kilogrammes of mercury were then siphoned off, and the leak again measured. More mercury was then siphoned off, and again the leak taken. This was continued until the leak was too large to measure. Smaller quantities of radium were then substituted for the larger quantity, and the absorption measurements continued till only 6 cm. covered the radium. At this stage a smaller lead electroscope, having a volume one-fifth of that of the larger, was substituted for it, and used for the absorption measurements from 1 to 6 cm. This was necessitated by the powerful nature of the source used. Experiments were conducted usually so that the leak was about 10 divisions per minute at the commencement, and about 1 division per minute or less at the end, of the range of thickness investigated. With the larger electroscope it was essential that the leaks should not be too great, owing to a possible lack of saturation in so great a volume of air. The results obtained are given in the table that follows: In the first column is put the range of thickness × density of mercury covering the radium. The values given are obtained directly from the weight of mercury and the dimensions of the pot. In the second column are put the values of the absorption coefficient divided by the density of mercury. All thicknesses in the tables which follow are given in centimetres, and all values of μ are μ cm.$^{-1}$.

Table II.

Range of thickness × density.	$\frac{\mu}{d} \times 100$.
14 to 72	4·39
44 102	4·34
100 140	4·36
136 225	4·39
132 307	4·39
Mean value 14 to 307	4·38

The values of μ/d were obtained as follows:—The logarithms of the ionisation were plotted against the product of thickness and density. On the average there was a point for every 12 units of thickness × density. From this straight line the mean value of μ/d over the range under investigation was obtained. Each of the five experiments was separately carried out, and is quite distinct from the other four. It is seen that the values of μ/d do not differ by more than about 2 per cent. over the entire range investigated.

Two examples showing how closely the exponential law of absorption holds are given in the two following tables. The first table deals with the first part of the range investigated, the second with the last part. In the first column of each table is given the absolute thickness × density of mercury over the radium, in the second the observed values of the ionisation, and in the third the calculated values. For convenience, the observed value of the ionisation for the smallest thickness × density is in both tables put at 1000. The theoretical values are obtained from the usual equation,

$$I_{t_2}/I_{t_1} = e^{-\frac{\mu}{d}(t_2 d - t_1 d)}.$$

Table III.—Range of Thickness × Density, 13·6 to 71·6.

$\mu/d = 4{\cdot}39 \times 10^{-2}$.

Thickness × density.	Observed ionisation.	Calculated ionisation.
13·6	1000	1000
21·6	700·4	697·9
30·3	479·7	472·9
38·5	330·9	335·5
46·9	229·5	232·1
55·1	160·8	162·0
63·4	111·9	112·6
71·6	78·4	78·5

Table IV.—Range of Thickness × Density, 131·9 to 307.

$\mu/d = 4{\cdot}39 \times 10^{-2}$.

Thickness × density.	Observed ionisation.	Calculated ionisation.
131·9	1000	994·2
143·2	607·4	605·6
156·7	330·0	335·1
170·0	187·4	186·9
183·7	101·6	102·4
196·7	57·79	57·95
208·7	34·24	34·24
219·6	20·51	21·24
234·2	11·41	11·19
243·7	7·48	7·38
256·6	3·97	4·19
272·5	2·05	2·09
307·0	0·47	0·46
323·0	<0·1	0·23

Since $\mu/d = 4{\cdot}38 \times 10^{-2}$ for mercury, and d is 13·59, $\mu = 0{\cdot}595$ cm.$^{-1}$. A thickness × density of 15·8, or a thickness of 1·164 cm. mercury, therefore, cuts the γ-rays of radium down to half value. Over the range 13·6 to 307 of thickness × density, the γ-radiation is reduced in the ratio of 360,000 to 1.

Under the conditions of experiment, the leak due to the γ-rays from 300 millicuries of emanation in the electroscope was 3·77 divisions per minute through a thickness × density of 183, and of 0·017 division per minute through 307. The radiation from 300 millicuries, if unabsorbed by mercury, would produce 10,800 divisions per minute in the electroscope. The radiation, capable of penetrating thicknesses greater than 22·5 cm. of mercury, is therefore less than 0·017÷10800, *i.e.* is less than $1{\cdot}6 \times 10^{-6}$ of the initial γ-ray beam.

The value of μ for mercury, 0·595 cm.$^{-1}$, is 7 per cent. less than a value given in a previous paper by Soddy and Russell.* In the former research the source of radium used was less than half a milligramme, and the absorption over the first 3 cm. only could be investigated.

The mean value of μ/d for mercury, $4{\cdot}38 \times 10^{-2}$ cm.$^{-1}$, is very similar to the mean value obtained in a previous research for a range of 2 to 22 cm. of lead, namely $4{\cdot}37 \times 10^{-2}$ cm.$^{-1}$. The results of this paper, both with regard to the absence of a very penetrating radiation, and to the absorption of the rays by an element of high atomic weight, confirm and extend the results previously obtained with lead as an absorbent. Beyond a thickness of 22·5 cm. of mercury it will be difficult to detect γ-rays even if large quantities of

* F. Soddy and A. S. Russell, 'Phil. Mag.,' 1909, vol. 18, p. 644.

radium are forthcoming. In the electroscope used in these experiments, the leak due to the γ-rays from 10 grm. of radium would be only 4 per cent. of the natural leak, after they had penetrated 28·5 cm. of mercury.

Summary.

(1) The γ-rays of radium C are absorbed by mercury over a range of thickness of 1 to 22·5 cm. strictly according to an exponential law. The mean value of μ/d is $4{\cdot}38 \times 10^{-2}$. Over this range the intensity is diminished in the ratio of 360,000 to 1.

(2) No trace of any radiation more penetrating than γ-rays could be detected. If any exists, and is capable of ionising air, its intensity is less than 2×10^{-6} of that of the initial γ-ray beam.

I have to express my warmest thanks to the Castner-Kellner Alkali Company of Runcorn for loaning me 800 lbs. of pure mercury, and for making for me the cast iron pot which contained it. But for their generosity in this matter, the present research could not have been carried out.

I have also to express my thanks to Prof. Rutherford, in whose laboratory this work was carried out, for his suggestions and advice.

On the Scattering and Absorption of Light in Gaseous Media, with Applications to the Intensity of Sky Radiation.

By Louis Vessot King, B.A. (Cantab.), Lecturer in Physics, McGill University, Montreal.

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(Abstract.)

Sections 1 *and* 2.—Lord Rayleigh* showed, in 1871, that when radiation travels through a medium containing small particles whose dimensions are small compared with the wave-length, each of these sets up a secondary disturbance which travels in all directions at the expense of the energy in the original direction.

Various hypotheses of the æther and of the molecule agree in giving for the scattered radiation near an element of volume an expression of the form

$$I(0, \theta) = \mu(\theta) E = \tfrac{1}{2}\pi^2 (n^2-1)^2 \lambda^{-4} (1+\cos^2\theta) E/N, \quad (1)$$

where $\omega I(0, \theta)$ is the intensity contained in a small solid angle ω in a direction θ with the direction of the original beam E; n is the refractive index of the gas, N the number of molecules per unit volume, and λ the wave-length of the incident radiation.

In a later paper Lord Rayleigh† gave reasons for believing that the molecules of a gas are themselves able to scatter radiation in this way, and that both the attenuation of light by the earth's atmosphere and the blue of the sky could be thus accounted for. These results were applied by Lord Kelvin‡ (1904) to the problem of sky radiation, and this seems to have been the most recent theoretical contribution to the subject.§ Recent observations on sky radiation seem to have thrown some doubt on the sufficiency of the simple Rayleigh law to account for facts. Seeing that

* Rayleigh, 'Phil. Mag.,' 1871, vol. 41, pp. 107, 274, 447; 'Collected Works,' vol. 1, pp. 87, 104, 518.

† Rayleigh, 'Phil. Mag.,' 1899, vol. 47, pp. 375—384; 'Collected Works,' vol. 2, pp. 397—405.

‡ Kelvin, 'Baltimore Lectures,' 1904, p. 311.

§ The writer is indebted to Dr. Otto Klotz, of the Dominion Observatory, Ottawa, for calling his attention to the work of Exner along these lines. Exner, 'Sitzungsbericht d. K. Akad. d. Wissen., Wien, M.-N. Klasse,' 1909, vol. 118, IIa. A summary of Exner's results is given by Abbot (C. G.), in his recent book, 'The Sun,' p. 299 (Appleton and Co., 1911).

the phenomenon of molecular scattering is now well established, the subject has a very wide scope of application to a great variety of astrophysical problems. It has therefore seemed desirable to investigate the subject in as general a manner as possible, and apply for verification to existing numerical data on absorption and scattering of radiation by the earth's as well as by the sun's atmosphere.

The two main extensions of the existing theory which form the basis of the present investigation are as follows:—

(i) The introduction of a second term in the differential equation for loss of intensity in a beam of radiation which allows for attenuation by absorption (without scattering), *i.e.* the absorption gives rise to a direct conversion of radiant energy in the æther into thermal molecular agitation in the gas. The introduction of this term leads to an equation of the form

$$E = E_0 e^{-(\alpha+\kappa)x} = E_0 e^{-Kx}, \quad \text{where} \quad K = A + B\lambda^{-4}, \tag{2}$$

and A and B are constants depending on the density of the gas. The existence and magnitude of the term A can then be inferred from observations on atmospheric attenuation, and in this way a numerical estimate made of the distribution of energy between the æther and the molecular velocities of the gas.

(ii) The second feature of the present investigation consists in the mathematical consideration of effects due to *self-illumination.* Suppose a mass of gas exposed to external illumination: as a result of scattering the whole mass of gas will be luminous as is the case in the earth's atmosphere. Thus each element of volume besides being subject to the external incident illumination is also subject to the scattered radiation from the entire volume, and this factor will add considerably to the scattered intensity from the element of volume. The mathematical expression of this effect gives rise to an *integral equation* which may be written

$$I(x, y, z, 0, \theta) = \mu(\theta) E(x, y, z) + \int_{\Sigma} \mu(\widehat{rr'}) r'^{-2} I(x', y', z', 0, \theta') e^{-\int_0^{r'} K dr'} dv'. \tag{3}$$

$I(x, y, z, 0, \theta)$ is the intensity of scattered radiation per unit solid angle in a direction θ with the incident radiation and emanating from an element dv of volume at the point (x, y, z). The accented symbols refer to the corresponding quantities with reference to another element of volume dv' at (x', y', z'). The exponential expresses the attenuation of the scattered radiation from dv' in travelling along r' to dv. The integral is taken throughout the volume enclosed by the surface Σ drawn so as to include the entire mass of gas. A differential equation for E completes the analytical

expression of the problem. The total scattered intensity received from a small solid angle ω in any direction is given by

$$\omega \mathrm{T} = \omega \int \mathrm{I}(x, y, z, 0, \theta) e^{-\int \mathrm{K}\, dr} dr, \tag{4}$$

where the integrals are taken so as to include all the elements of volume in the small solid angle.

The importance of self-illumination on the intensity of sky radiation is recognised both by Kelvin and Rayleigh, although no attempt seems to have been made to calculate its effect. Schuster* in a paper on "Radiation through a Foggy Atmosphere" draws attention to the importance of the effect in astrophysical problems and obtains a representation of its magnitude by means of differential equations; the results are applied to problems of the reversal of lines in certain stellar spectra to be attributed to absorption and scattering in the stellar atmospheres. The application of the theory of integral equations to problems of this type seems to offer a means of attacking a great number of physical problems.

Section 3.—An immediate application of the general equations just discussed can be made to the problem of absorption and scattering of solar radiation by the earth's atmosphere. The general integral equation can in this application be reduced to one in a single variable and by means of a perfectly general transformation of variables can be further reduced to the case of a homogeneous atmosphere contained between two parallel planes at a distance H apart. This transformation is independent of any law of density or temperature gradient in the atmosphere and only requires that planes parallel to the earth's surface be planes of equal density. The integral equation for the scattered radiation can then be written down, and by a consideration of the rate of accumulation of energy in an element of volume the result is shown to be consistent with the well-known law of attenuation,

$$\mathrm{E}(\mathrm{X}) = \mathrm{S} e^{-\mathrm{K}_0 (\mathrm{H}-\mathrm{X}) \sec \zeta}, \tag{5}$$

$\mathrm{E}(\mathrm{X})$ being the intensity of solar radiation of wave-length λ reaching a level X; S is the intensity outside the earth's atmosphere and ζ is the zenith distance of the sun; K_0 is the generalised coefficient of attenuation in equation (2) referred to normal pressure and density.

Section 4.—Progress towards the solution of the integral equation requires the development of a special method of approximation. It is shown in a general case that the solution must lie between two limits called the *extreme solutions*, and an intermediate value called the *mean solution* is obtained which

* Schuster, 'Astrophys. Journ.,' January, 1905, vol. 21, p. 1.

represents a value probably not far from the correct one in the applications considered.

Section 5.—The approximate solution of the integral equation leads to a number of transcendental functions which recur so frequently that they are designated by a special notation and tabulated; among these are

$$\left.\begin{aligned} G(x) &= (1-e^{-x})/x, \\ f(x) &= x\int_x^\infty e^{-u}u^{-2}du = e^{-x}+xEi(-x) = -\int_x^\infty Ei(-u)\,du, \\ B(x) &= Ei(-x)-\log x, \qquad B(-x) = Ei(x)-\log x, \end{aligned}\right\} \quad (6)$$

where $Ei(-x)$ is Glaisher's* *exponential integral*, denoted by

$$Ei(-x) = -\int_x^\infty u^{-1}e^{-u}\,du.$$

Section 6.—The intensity of sky radiation corresponding to any direction of sun and sky can now be obtained in terms of the coefficient of attenuation for a particular wave-length. Formulæ are developed giving the total sky radiation on a horizontal plane and rough estimates of the degree of polarisation of the light from different regions of the sky.

Section 7.—Numerous observations on the attenuation of solar radiation have been made by the Smithsonian Astrophysical Observatory† in connection with the determination of the solar constant. At any station at a height x above sea-level the law of attenuation may be written

$$E(x) = Se^{-C\sec\zeta . p/p_0} = Se^{-C_x\sec\zeta}, \quad (7)$$

where $C_x = Cp/p_0$ and $C = \beta\lambda^{-4}+\gamma$; β and γ are constants for all stations and have the values $\beta = \frac{32}{3}\pi^3(n_0-1)^2H/N_0$ and $\gamma = \alpha_0H$, while H is the height of the "homogeneous atmosphere."

The term γ expresses the attenuation by absorption alone. If the observed values of the coefficients of attenuation C_x are plotted against the inverse fourth power of the wave-length for different stations we should obtain a family of straight lines all passing through the same point. The coefficients of attenuation for Mount Whitney (4420 metres), Mount Wilson (1780 metres), Potsdam (100 metres), and Washington (10 metres), are analysed in this way; the result gives rise to a family of straight lines shown in the diagram.

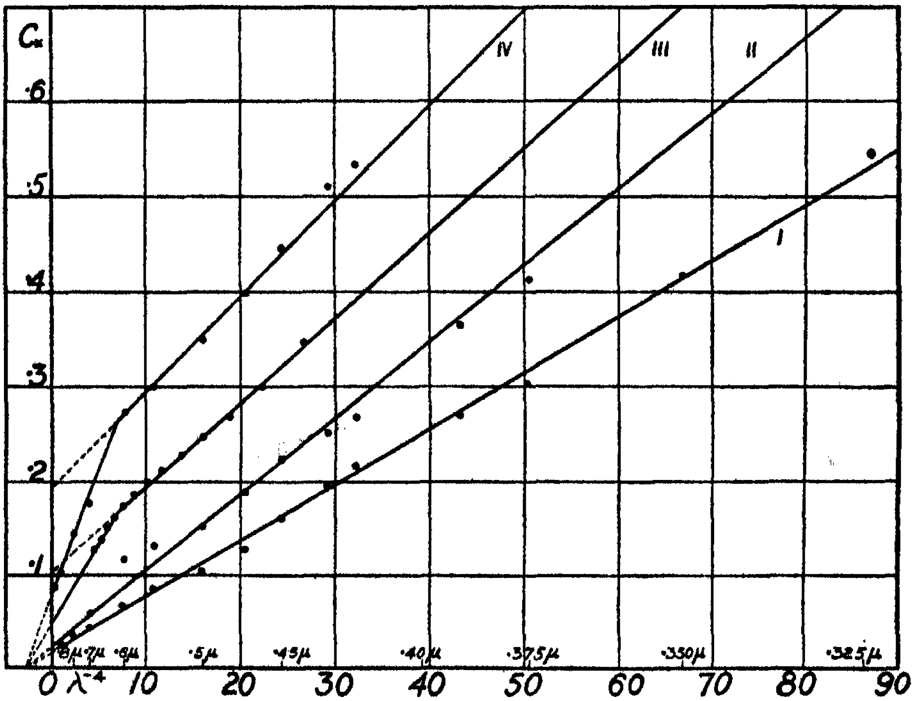
The results for sea-level stations require special interpretation owing to

* Glaisher, 'Phil. Trans.,' 1870, p. 367.

† A summary of the most recent results of the Smithsonian Astrophysical Observatory is given by Abbot (C. G.), "The Sun's Energy, Spectrum, and Temperature 'Astrophys. Journ.,' October, 1911, vol. 34.

the effect of "atmospheric dust." A discontinuity in the straight lines occurs in the neighbourhood of $\lambda = 0{\cdot}610\,\mu$. Wave-lengths greater than this constitute *long-wave radiation,* while shorter wave-lengths constitute *short-wave radiation*; the two classes demand separate discussion.

(i) *Long-wave Radiation.*—For the longer waves the "dust" present in the atmosphere is able to absorb as well as to scatter: the fact that the straight lines intersect in the same point leads to the result $\beta/\gamma = \beta''/\gamma''$ independently of any law of distribution of "dust": the presence of "dust"



Variation of Coefficients of Atmospheric Attenuation with Wave-Length.

Curve I.—Mount Whitney. II.—Mount Wilson. III.—Potsdam. IV.—Washington.

gives rise to the constants of absorption and scattering denoted by accented letters. This result can be expressed in the form: the ratio of energy scattered to energy absorbed and converted into heat is constant for any wave-length and is independent of the nature of the scattering particle whether "dust" or molecules.

(ii) *Short-wave Radiation.*—In this case we may suppose that "dust" attenuates radiation of all wave-lengths without scattering, so that the scattering which exists is due entirely to air-molecules. In order to test this conclusion we measure the slope of the straight lines of the diagram over the

portion corresponding to short-wave radiation, and so obtain values of β, the barometric pressures at the stations being supposed known at the time of observation. From a knowledge of the optical constants of air, we may make use of these values of β to obtain an estimate of N_0, the number of molecules per cubic centimetre of a gas at standard temperature and pressure. The results are as follows :—

$$\left.\begin{array}{llll}\text{Potsdam......} & N_0 = 2{\cdot}51\times10^{19}, & \text{Mt. Wilson ...} & N_0 = 2{\cdot}28\times10^{19} \\ \text{Washington} & N_0 = 2{\cdot}24\times10^{19}, & \text{Mt. Whitney...} & N_0 = 2{\cdot}26\times10^{19}\end{array}\right\} \quad (8)$$

These are in tolerable agreement with the values obtained by Rutherford and Geiger* ($2{\cdot}72\times10^{19}$) and by Millikan† ($2{\cdot}644\times10^{19}$).

Another numerical result of some interest is obtained from the observations on attenuation of solar radiation in the comparatively dust-free air above Mount Wilson and Mount Whitney. From the straight lines in the diagram we find

$$\gamma = \alpha_0 H = 0{\cdot}032, \quad \text{so that} \quad \alpha_0 = 4{\cdot}0\times10^{-8}\,(\text{cm.})^{-1}. \tag{9}$$

α_0 represents the fraction of radiant energy travelling through air at normal pressure and temperature, which is converted into thermal molecular agitation per centimetre of path. If direct sunlight is travelling through air under these conditions, the above value of α_0 leads to an increase of temperature of $0{\cdot}015°$ C. per hour. The effect of "dust" as at Washington is to increase this value about six-fold.

Section 8.—The intensity of sky radiation can be calculated in terms of the coefficients of attenuation; the results for zenith sky are calculated for Mount Wilson for comparison with observations, and for Washington as typical of a sea-level station. The former results agree as regards both quality and total intensity of sky radiation sufficiently well with experiment to indicate that molecular scattering when taken in conjunction with self-illumination is sufficient to account for all the phenomena of sky light. The hitherto neglected factor of self-illumination is responsible for about 33 per cent. of the whole effect at $0{\cdot}410\,\mu$ in the violet and for about 5 per cent. at $0{\cdot}741\,\mu$ in the red.

Sky intensities at sea-level are interesting in enabling us to calculate the total radiation from the sky on a horizontal surface, a magnitude of some importance in meteorology. At Washington it is found that this quantity is about 7·8 per cent. of the normal solar radiation reaching the earth, and is approximately constant for all zenith distances of the sun. Thus, if the sun's zenith distance is 60°, the contribution of sky radiation to the heat available

* Rutherford (E.) and Geiger (H.), 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 171.

† Millikan (R. A.), 'Phys. Rev.,' April, 1911, vol. 32.

for heating the earth is 16 per cent. of the sun's heat; for a zenith distance of 70° the proportion is 24 per cent., and for 80° the proportion reaches 44 per cent. Sky radiation is thus a feature of some importance in the meteorology of northern latitudes where the altitude of the sun remains small during the winter months.

Summary.—The analysis of the present investigation seems to support the view that, at levels above Mount Wilson, molecular scattering is sufficient to account completely both for attenuation of solar radiation and for the intensity and quality of sky radiation. Even at sea-level the effect of "atmospheric dust" can be taken into account in a simple manner in the formulæ for absorption and scattering. Should future observations support the validity of the simple law expressed by equation (2) connecting the coefficient of attenuation with the wave-length, we may with considerable assurance make use of the law to obtain the coefficients for very short or very long wave-lengths when the direct method of calculation from high and low sun observations leaves room for considerable uncertainty owing to the small intensities in the solar spectrum at these wave-lengths, and owing to other experimental difficulties. Schuster (*loc. cit.*) points out in this connection the extreme importance of determining accurately the form of the solar intensity curve outside the earth's atmosphere for short wave-lengths, since the effect of a solar atmosphere in absorbing and scattering radiation is to give rise to an intensity-curve which does not agree with that given by Planck's formula, especially for short wave-lengths.

Absorption and scattering of radiation by the sun's atmosphere, taken in conjunction with effects of self-illumination, constitutes a problem analogous to that just considered for the earth's atmosphere. By making a comparison between the calculated variation of intensity of radiation of different wave-lengths over the solar disc and the results of observation it will be possible to determine from the intensity-curve of the normal solar spectrum outside the earth's atmosphere the intensity-curve at the radiating layer of the sun. This corrected curve may then be compared with that given by Planck's formula, and a closer approximation made to the temperature of the sun than the values now given. This investigation the writer hopes to be able to deal with in a future communication.

Some Electrical and Chemical Effects of the Explosion of Azoimide.

By Rev. P. J. Kirkby, M.A., D.Sc., and J. E. Marsh, M.A., F.R.S.

(Received November 23, 1912,—Read January 16, 1913.)

Introduction.—In a paper* published some years ago, the amount of electricity liberated by exploding electrolytic gas ($2H_2+O_2$) at certain pressures was measured and compared with the number of molecules of water formed by the explosion. It was found that about 10^7 molecules of water were formed for every pair of gaseous ions that reached the electrodes, and that the energy required to produce the observed quantity of electricity was an extremely small fraction of the energy set free by the explosion.

The present investigation was undertaken to see whether these results would be substantially modified in the case of the explosion of azoimide (HN_3). The explosion of this gas differs from that of electrolytic gas in two important particulars from the point of view of these experiments. In the first place it is disruptive, and secondly it is not productive of water-vapour, which with its well-known influence upon the motion of gaseous ions may, by promoting their re-combination, greatly obscure the electrical effects of the explosion.

Method of Research.—The method consisted in exploding the gas at various low pressures between two electrodes charged to a potential difference and in measuring the quantity of electricity thrown on to one of the electrodes. Then, the volume of the gas contained between the electrodes being known, and its pressure, it is easy to find the ratio between the number of pairs of gaseous ions that find their way to the electrodes and the total number of molecules of the gas disrupted.

Preparation of the Azoimide.—The gas was generated by admitting dilute sulphuric acid into an exhausted vessel containing barium azoimide. The latter (BaN_6) was prepared in the following way. Nitrous oxide was passed over sodamide at the temperature 190° C. The product of this reaction was dissolved by water, and excess of sulphuric acid was added to it. From this solution the azoimide was distilled into barium hydroxide, forming barium azoimide, the excess of barium hydroxide was precipitated by carbon dioxide, and the solution after filtering was evaporated to dryness. The residue was redissolved in water to remove a small amount of carbonate, and on evaporation the pure salt was obtained, which after drying was analysed;

* C. E. Haselfoot and P. J. Kirkby, 'Phil. Mag.,' October, 1904.

0·9294 grm. of the salt gave 0·9688 grm. of $BaSO_4$, from which numbers the percentage of barium was found to be 61·3 (calc. BaN_6 61·9).

Description of the Apparatus.—The salt (BaN_6) having been thus prepared, about a gramme was placed in a small vessel C, illustrated in fig. 1, which shows the apparatus in diagrammatic form. E is a drying vessel containing calcium chloride, G is a vessel for receiving the gas and I is a U-tube manometer, which when the tap J was opened was in connection with the little explosion chamber S. The tube T was connected with a Fleuss oil-pump. To generate the gas, normal solution of sulphuric acid in excess of the salt in C was placed in the funnel A, and with all the taps open except B

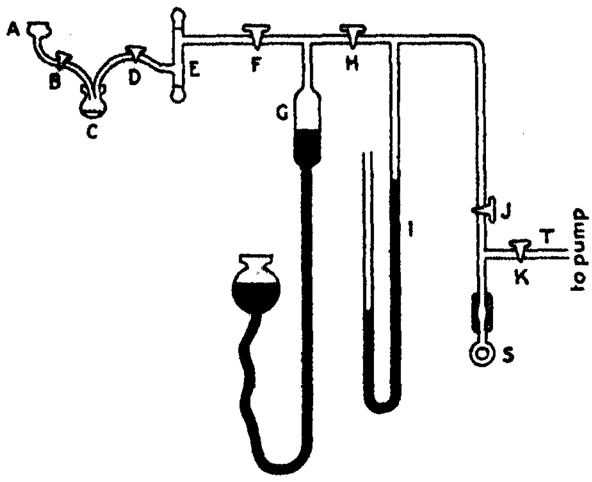


Fig. 1.

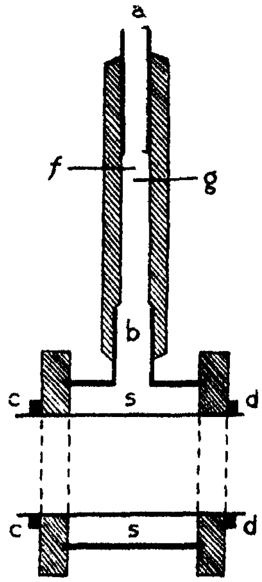


Fig. 2.

the air in C was pumped out; D was then closed and the sulphuric acid admitted through B, and the reaction having been accelerated by surrounding C with hot water, the gas produced was dried in E, collected in G and sometimes pressed back into E for further drying. Before an experiment S was exhausted by the pump and azoimide admitted and then immediately exploded. The object of the tap J was to economise the gas.

The explosion chamber S, which consisted principally of two co-axial cylinders separated by ebonite, is illustrated in fig. 2, drawn to scale, which represents a section of it by a plane through the axis of the cylinders. The shaded parts of the diagram represent ebonite: *a* is the end of a glass tube leading to the apparatus just described, *b* is a brass tube leading to the

space s between the co-axial cylinders. These cylinders, which were of gilded brass, were insulated from one another by means of two blocks of ebonite, through which the inner cylinder passed, the brass rings c, d, serving merely to prevent the ebonite from being displaced by the explosion. The spark-gap is between the thick aluminium wires f and g, which are fixed in an ebonite sleeve fitting the tubes a, b, accurately. All the joints were made with black elastic glue.

The outer diameter of the inner tube was 2·23 cm., and the inner diameter of the outer tube was 3·33. The length of the outer tube was 3·02 cm. Hence the volume between the electrodes was 14·5 c.c.

Electrical Arrangements.—These were very simple. The outer cylinder was connected to one of the Oxford City mains (voltage about 105), and the inner through a low resistance ballistic D'Arsonval galvanometer to the other main. The spark-gap terminals f and g were connected to the ends of a small induction coil.

Method of Experiment.—The explosion chamber was exhausted by the oil pump to as low a pressure as possible. (The "vacuum" attained was about 2 mm. or less, most of the residual pressure being most probably due to water-vapour.) Then the gas was admitted from the adjoining chamber and exploded, and the resulting throw of the galvanometer determined. It was verified that no part of the throw was due to the sparking.

Results.—The results of three series of experiments are given in the following tables, a "series" being a number of experiments carried out continuously in the order given upon the same sample of gas. In every case recorded in the tables the difference of potential of the cylinders was nearly 105 volts.

Notation of the Tables.—

p = the pressure of the gas in millimetres of mercury.
Q = the observed quantity of electricity in micro-coulombs.
μ = the number of molecules of gas exploded divided by the number of pairs of ions that reach the electrodes.

(It is easy to prove that $\mu = 7{\cdot}8 \times 10^4 p/Q$ by means of the well-known equation $Ne = 1{\cdot}22 \times 10^{10}$, where N is the number of molecules of a gas in 1 c.c. at 760 mm. pressure and 15° temperature, and e is the charge on an electron in electrostatic units; for the volume of gas exploded between the electrodes was 14·5 c.c.)

Previous to the series of experiments in Table I the gas had been dried (in the vessel E of fig. 1) by contact with calcium chloride for 24 hours. The first explosion at the pressure 151 mm. produced much more electricity

Table I.

p.	Q.	$\mu \times 10^{-5}$.	Outer cylinder.
151	69·5	1·69	+
117	11·0	8·3	+
151	10·5	11·2	+
108	11·0	7·7	−
55	6·3	6·8	−
39	4·7	6·5	−
28	4·7	4·6	−
19	5·9	2·5	−
15	4·9	2·4	−
10	No explosion		−

than the rest, and seven times the amount produced by the third explosion under apparently the same conditions. It is impossible to attribute this to any extra dryness; it is an instance of a curious phenomenon repeatedly observed, consisting in the production, not necessarily at the first explosion, of an abnormal amount of electricity for no apparent reason. Each of the three tables given shows an instance of it.* Thus in Table II at the pressure 82 mm. the value of Q is 59, and in Table III, pressure 214 mm., the value of Q is 87. In both these latter cases the throw of the galvanometer was so large that only a rough estimate, noted as less than the true value, was possible.

Table II gives another series of experiments upon azoimide after it had been allowed to remain a few minutes over phosphorus pentoxide in a little

Table II.

p.	Q.	$\mu \times 10^{-5}$.	Outer cylinder.
12·0	No explosion		−
40·0	6·0	5·2	−
82·0	59·0	1·1	−
30·5	7·6	3·1	−
20·0	5·9	2·6	−
13·0	5·0	2·0	−
8·5	No explosion		−
65·5	7·6	6·7	+
40·5	3·7	8·5	+
25·0	2·5	7·8	+
16·0	1·9	6·6	+
11·0	1·2	7·1	+
8·0	No explosion		+

* The same effect was observed in the explosion of $2H_2+O_2$ (*loc. cit.*), and though this was thought to be due to a higher degree of dryness, yet prolonged attempts to dry the gas wholly failed even approximately to reproduce the greater quantities of electricity observed.

vessel between the taps H and J, so that it was probably drier on explosion than in other cases. It is clear though, by comparing Table II with Table I, that this additional drying made no perceptible difference.

The observations recorded in Table II made with outer cylinder positive exhibit a rough constancy in μ (7×10^5 or 8×10^5), independent of the pressure. This table also appears to show that at the lower pressures more electricity resulted from an explosion when the outer cylinder was negative than when it was positive. *This latter conclusion is also supported by Table I, in which the values of* μ, when the outer cylinder was negative descend from $6{\cdot}8 \times 10^5$ ($p = 55$) to $2{\cdot}4$ ($p = 15$), which last agrees with the values of μ in Table II corresponding to a negative outer cylinder.

It does not seem possible to account for this conclusion by means of any known effects. If the pressure were lower and the inner cylinder much smaller it would be easy to do so. For in that case, if the inner cylinder were positive, the negative ions in moving towards it would pass through the intense field of force surrounding it and so would generate others by collision; whereas, if the inner cylinder were negative, the positive ions in passing through the similarly intense field would produce no appreciable similar effect.* In the present case, however, the field of force was of the same order of intensity between the cylinders. Its value at the inner cylinder was 236 volts per centimetre, and at the outer 186. Now, for a given ratio of electric force to pressure, the number of ions generated by the collisions of an electron per centimetre of its motion is proportional to the pressure of the gas.† It is clear, therefore, that if the increase in the values of Q at the lower pressures, when the outer cylinder was negative, were due to collision effects, aggravated by the abnormal condition of the gas, an increase of the same order would have been observed at the lowest pressures with a positive outer cylinder. In fact, in some cases the ratio of electric force to pressure near the outer cylinder, when that cylinder was positive and no increase in the value of Q was observed, exceeded the same ratio near the inner cylinder when, the inner cylinder being positive, a striking increase was observed. (See Table II, pressures 20, 11, where the ratio in question, applying to the region close to the positive electrode, through which all negative ions had to pass, was 12 and 17 *q.p.*)

Effect of Introducing a Resistance.—The effect of introducing a resistance between one end of a battery and one of the cylinders is shown in Table III.

* J. S. Townsend, 'Ionisation of Gases by Collision,' p. 11 f.; or P. J. Kirkby, 'Phil. Mag.,' February, 1902.

† Townsend, *ibid.*, p. 18.

Table III.

(Outer cylinder connected through resistance R to the positive pole.)

p.	Q.	R.	$\mu \times 10^{-5}$.
		ohms.	
124	2·2	10^6	44·0
63	2·9	10^4	17·0
43	0·7	10^5	48·0
80	2·5	0	9·3
214	87·0	0	1·9
152	12·3	0	9·6
217	27·2	0	6·3

The effect is very marked. The explanation is, probably, that the electric force between the cylinders is reduced to such an extent during the passage of the current, when there is a considerable resistance, that the amount of recombination of ions is greatly increased, and the quantity of electricity that reaches the electrodes thereby greatly diminished. In fact, the difference of potential of the electrodes is diminished by CR volts when the current C ampères is flowing; and it is not difficult to show that CR approximated to the voltage V of the battery, *i.e.* the voltage difference of the cylinders when no current was passing. To show this, let us suppose that the quantity Q (micro-coulombs) observed was carried in time t by a stream of ions of constant density and constant velocity u to one electrode. Then, if d denotes the distance between the electrodes, $t = d/u$ and $C = Q \times 10^{-6} u/d$. Now, the electric force under which the ions moved was, roughly, $(V - CR)/d$. Hence

$$u = \frac{760}{p} \frac{V - CR}{d} u_0,$$

where u_0 is the velocity of the ionic stream moving under 760 mm. pressure and 1 volt per centimetre. Therefore

$$C = Q \times 10^{-6} \times 760 (V - CR) u_0/pd^2. \qquad (a)$$

This equation (since $d^2 = 0·3 q.p.$) makes the ratio V/CR equal to

$$1 + \frac{1}{4·5 u_0}, \qquad 1 + \frac{1}{1·2 u_0}, \qquad 1 + \frac{1}{4·1 u_0}, \text{ respectively,}$$

in the case of the first three observations of Table III. Now u_0 is probably greater than, and cannot be much less than, unity*; therefore V − CR is substantially less than V. This result has been obtained on the assumption that the current was constant and the field of force undisturbed by the flow of ions. But the conclusion at least indicates that in the actual case CR

* See Sir J. J. Thomson's 'Conduction of Electricity through Gases.'

became comparable to V in the course of the discharge, and the voltage difference of the cylinders sufficiently reduced to account for the small values of Q.

Hence the smaller values of Q observed when a resistance was in the circuit may be attributed to the reduced difference of potential between the electrodes, which permitted a greater amount of recombination to take place.

But it does not follow that when the resistance was absent there was no recombination. For the above equation (a) shows that the current, if assumed to be uniform, was throughout of the order of magnitude $10^{-1}u_0$ when $R = 0$, so that it was quite large enough to produce polarisation of the electrodes, involving recombination.

General Conclusion.—The general result of these experiments is to show that the number of pairs of ions generated by an explosion of azoimide is exceedingly small compared with the number of molecules dissociated by the explosion. The observed proportion is so small (always less than 1 to 100,000) as to lead to the conclusion that dissociated atoms do not in general carry electrostatic charges; for, if in general they are charged, it is difficult to see how recombination could be so complete in such a strong field of force as in the present case—a field which would impart a high velocity to such electrified atoms. The same conclusion can be drawn from the experiments already alluded to on the electrical effects of exploding electrolytic gas in a field of force.* In fact the latter effects are not so great as the effects of exploding azoimide.†

What then is the explanation of the formation of ions during the explosion? The explanation is probably to be found in the mutual collisions of the dissociated atoms as they unite in forming the product of the explosion. The energetic nature of those collisions is shown by the evolution of heat. Under favourable conditions of impact, including a sufficiently high relative velocity, ionisation may take place, just as Townsend has shown that a positive ion, which is either of atomic or molecular dimensions, is capable under such conditions of impact of breaking up a molecule which it strikes into ions.‡

* See also P. J. Kirkby, 'Roy. Soc. Proc.,' 1911, A, vol. 85, where a definite proof is given that separated atoms of oxygen are uncharged.

† A comparison of the two greatest effects observed in exploding HN_3 and $2H_2+O_2$ makes the number of ions, per gramme-molecule of each gas exploded, just 100 times greater in azoimide than in electrolytic gas. It is possible, however, that the battery used in the experiments upon the latter gas may have been earthed through a resistance (100,000 ohms or less), in which case the electrical effects may have been greater than they were observed to be.

‡ Townsend, 'Ionisation of Gases by Collision,' p. 38.

Lowest Pressure of Explosion.—The lowest pressure at which azoimide was observed to explode in the apparatus described above was 11 mm. No explosion took place at pressures of 10 mm. or less. Observations made with different specimens of the gas were very consistent in this respect. Hence 10·5 mm. was very nearly the pressure-limit of explosions. This limit would probably be lower still for pure azoimide. For, in view of the imperfect evacuation of the oil pump, it cannot be asserted that more than 80 per cent. of the gas at the pressure 10 mm. was azoimide.

In this respect azoimide presents a sharp contrast with electrolytic gas, which does not explode at pressures much below 80 mm.,* a contrast that illustrates the highly explosive nature of azoimide. This striking difference might, perhaps, be modified if electrolytic gas were exploded when not drier than the azoimide was. But the contrast in any case would be great, for electrolytic gas was found† to combine under the electric discharge with perfect regularity at the pressure 39 mm., so that even when mixed with water-vapour its pressure of explosion must exceed 39 mm.

It is natural to conclude from these two cases that all explosive gases cease to explode even partially when their pressure is below a certain critical pressure, depending, of course, upon their temperature. The explanation is probably that the heat radiated from the molecules, formed as the product of the explosion in that region of the gas where the explosion originates, plays an important part in exploding the adjacent portions of the gas, namely, by raising its temperature and thus facilitating its disintegration by molecular or atomic collisions. If that is the case, when the pressure is reduced below a certain point, the molecules will be so far apart that the intensity of this radiation, diminishing as the inverse square of the distance, will cease to have the same effect, and the reaction will not be propagated.

It should be added that the least pressure at which explosion occurs seems to depend partly on the apparatus and partly on the manner of starting the explosion. Thus in one apparatus consisting of two brass discs about 7 cm. in diameter, and insulated from each other by an ebonite ring about 5 mm. thick, the azoimide did not explode by the heating of a platinum wire fixed between the discs until a pressure of over 200 mm. was reached, when the gas exploded with great violence, wrecking the apparatus and destroying the adjacent vessel in which a supply of azoimide had been collected over mercury (G, fig. 1).

Absorption of Azoimide by Phosphorus Pentoxide.—The first efforts to dry

* Haselfoot and Kirkby, *loc. cit.*

† P. J. Kirkby, 'Phil. Mag.,' January, 1905, p. 182.

azoimide over phosphorus pentoxide were not successful. The gas was absorbed as fast as it was admitted to the drying vessel. This effect, however, was greatly diminished by the substitution of fresh phosphorus pentoxide, which was carefully introduced into the drying vessel so as to be as dry as possible. It was found, however, that eventually this substance also absorbed azoimide with great rapidity. It follows that azoimide is absorbed by one of the phosphoric acids, into which P_2O_5 is partly transformed by the absorption of water-vapour, but is not absorbed by pure P_2O_5.

Formation of Crystalline Copper Azoimide on the Sides of the Explosion Chamber.—When the series of explosion experiments was finished and the explosion chamber opened, it was found that part of the gold surface had been attacked. In the part which lay in the direct line of fire from the ignition point the surface was covered with a dark-coloured deposit. The rest of the gold was bright. The small amount of the deposit rendered a quantitative analysis impracticable. A little scraped off the side was found to be transparent and crystalline when examined under the microscope. When held in the flame it exploded with a green-coloured flash. It was apparently not acted on by water, but hydrochloric acid dissolved it. This solution was found to contain azoimide, which was recognised by its characteristic smell and by giving, when distilled into silver nitrate solution, a white explosive precipitate. The solution did not contain gold, but copper in the cupric state was recognised by the ordinary tests. A cupric azoimide is thus formed in the explosion chamber. It seemed surprising that an explosive substance could be formed under such conditions and could survive after a long series of subsequent explosions.

A hydrated cupric salt of azoimide has been obtained by Curtius (the discoverer of azoimide) and Rissom.* It is precipitated on mixing a solution of a salt of azoimide with a solution of a cupric salt, and has a reddish-brown colour. Curtius and Rissom describe it as crystalline and highly explosive, even when moist, "eines der gefährlichst zu handhabenden Salze des Stickstoffwasserstoffs." It was not obtained by them free from water, even when kept in a desiccator.

Azoimide does not attack gold, nor when dried by calcium chloride does it appreciably attack clean brass. But in presence of air and water-vapour it attacks brass with the formation, after a few hours, of a black deposit which explodes with a green flash and dissolves in ammonia with a blue colour. This deposit is undoubtedly a cupric azoimide, but, as formed in this way, it is not crystalline and transparent, but amorphous and opaque, very different from the deposit in the explosion chamber. Copper is also

* 'Journ. Pr. Chem.' (2), vol. 58, p. 261.

attacked by moist azoimide vapour, giving the same black deposit. Zinc also is not attacked by dry azoimide, but in the moist gas it gives a white deposit which explodes with a bluish-white flash.

We have now to consider how the cupric azoimide comes to be formed in the explosion chamber. In the first place, it is unlikely that the formation is due to the action of the azoimide before explosion, since azoimide does not attack gold and hardly attacks brass when dry.* Nor is it likely that the gold helped the azoimide to attack the brass; otherwise the whole of the gold surface would have been attacked, whereas a considerable portion was bright and free from deposit. Moreover, no diminution in volume was noticed when the charges of azoimide were admitted into the explosion chamber. For the same reasons the explanation is precluded that the gold coating was ripped off by the first explosions, and that the azoimide then attacked the exposed brass. The deposit, moreover, was crystalline, while that formed slowly on brass by exposure to moist azoimide was found to be amorphous, though it is, perhaps, possible that an amorphous deposit formed in the first instance might be hammered into crystals by a series of explosions.

It seems, on the whole, most probable that the copper azoimide was formed during the actual explosions, and itself escaped explosion owing to its comparative stability, and to the fact that it was in contact with metal which would easily absorb the energy of subsequent explosions. From the above description given by Curtius and Rissom of the hydrated copper salt, it would appear that the salt obtained by explosion is much more stable than the one they observed, and this may be due to its being the anhydrous salt.

If, then, copper azoimide is formed by the explosions, it follows that a fair degree of stability belongs to the group N_3. Hence it is not unlikely that the first stage of the explosion is to break up HN_3 into H and N_3, some of the N_3 groups escaping further decomposition by being driven through the gold into combination with the copper. It might be supposed that the N_3 groups, being the same as the electrolytic chemical ions, were the cause of the electrical effect. But this is improbable, since the quantity of copper azoimide formed, though small, was much larger than could be accounted for by the very slight electrical effect on the assumption that every N_3 carried the atomic charge.

* An absorption of azoimide was noticed by us when a brass explosion chamber was used, instead of the gilded one. This absorption was, no doubt, due to the presence of oxide or other impurity on the brass. No absorption was ever noticed with the gilded brass even after many explosions had been made with it, when some of the gold surface may have been torn off.

On a New Method of Measuring the Torque produced by a Beam of Light in Oblique Refraction through a Glass Plate.

By Guy Barlow, D.Sc.

(Communicated by Prof. J. H. Poynting, F.R.S. Received November 29, 1912,—Read January 16, 1913.)

In a recent paper* an experiment was described in which the torque exerted by a beam of light in passing obliquely through a cube of glass was measured directly by the twist produced in the suspending quartz fibre. Since the light was incident at a constant angle, about 42°, the resulting torque was constant also, and the method may therefore be termed statical. Another form of the experiment, which we might call the dynamical method, will now be described.

Consider a parallel beam of light having energy H_1 per unit length, and let it pass through a parallel plate of glass of thickness a and refractive index μ. If the angle of incidence θ is small, the beam will be displaced laterally through a distance $a(1-\mu^{-1})\theta$, and on the assumption that the beam possesses momentum of amount $H_1 \div$ (velocity of light) per unit length, it at once follows that the torque produced should be $H_1 a(1-\mu^{-1})\theta$. Hence according to theory the torque is directly proportional to θ, and always tends to increase θ. If the plate has a moment of inertia I and is suspended vertically by a quartz fibre giving a torsion couple λ per radian, the action of the light will virtually decrease the restoring torque due to the fibre with the result that the natural period of small oscillations $T = 2\pi\sqrt{(I/\lambda)}$, will be altered to $T' = 2\pi\sqrt{(I/\lambda')}$, when the plate is traversed by the light, where $\lambda' = \lambda - H_1 a(1-\mu^{-1})$. Hence for the ratio of the periods we find

$$T'/T = \{1-H_1 a(1-\mu^{-1})/\lambda\}^{-\frac{1}{2}}.$$

In practice the change in period is very small, so putting $T'-T = \delta T$ we obtain

$$\delta T = H_1 a(1-\mu^{-1})T/2\lambda.$$

We can regard this result as giving us a new method of verifying the existence of the torque exerted by light, since it will suffice for the purpose if, instead of measuring the torque for any given angle, we compare the value of δT calculated as above with the value actually observed as obtained from the periods with the beam of light respectively traversing the plate

* Barlow, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 1.

and cut off. Further verification of the torque may seem unnecessary, but as this method possessed some novelty I have thought it worth while to make the experiment which is here described.

The above calculation shows that $\delta T/T$ should be proportional to $H_1 a$, the energy corresponding to the volume traversed in the plate. The former apparatus using a cube of 1 cm. edge was, therefore, quite suitable for the new experiment. With the strongest beam available the expected value of $\delta T/T$ was not more than $\frac{1}{8}$ per cent.; it was therefore evident that this dynamical method could not compare favourably with the statical as regards the accuracy obtainable. However, the new method possesses the distinct advantage that no especial care is needed either in adjusting the cross-section of the beam or in setting the angle of incidence. Theoretically we might double the effect by returning the beam from a fixed mirror, and again double it by employing a second beam traversing the cube at right angles to the first, but those devices would be objectionable in practice.

The above result must be modified on account of the reflection from the faces. The transmitted beam is weakened in intensity, and the two reflected beams give rise to torques also proportional to θ. If we take the reflection coefficient of the glass as 0·0042 for normal incidence it can be shown that the factor 0·831 must be applied to the expression for δT if H_1 is to refer to the *incident* beam.

The apparatus used was exactly the same as in the earlier experiment (*loc. cit.*). The cube was set normally to the light, and the section of the beam was then reduced to a square of about 9 mm. edge in order to give good clearance. The experiments were made with hydrogen at a pressure of about 10 cm. Hg. in the experimental case, as these conditions were known to be favourable for avoiding the effects of gas action. To test the elimination of disturbing effects the cube was allowed to come to rest and then exposed to the beam for several minutes, but no appreciable deflection was ever observed. Small torsional oscillations of the cube were conveniently set up by gently pumping out a little gas, or by letting a little more in. The transits of the centre of swing, occurring at intervals of 54 seconds, were observed for an hour and recorded on a chronograph. These transits consisted of 5 sets of 12, the sets 1, 3, and 5 being taken with the light off, the alternate sets 2 and 4 with the light on. The damping reduced the amplitude to 1 per cent. of its initial value in the course of one hour, so that the time of observation could not be usefully extended. The mean periods T and T′ for the alternate sets were obtained by applying Gauss's method—thus each set gave six independent values of the period. Finally, δT was obtained by taking the difference between the mean period for a set with

light on, and the mean period, with light off, for the sets before and after. This treatment eliminates any error due to a possible effect of amplitude or temperature variation on the period of the cube. The torsion head was rotated so that all four sides of the cube were used *in* succession as incident faces. The results are given in the following table :—

	T.	T′.	T′−T = δT.	Mean δT.
1st face	107·621 ·614 ·619	107·782 ·782	0·165 0·165	0·165
2nd face	·638 ·642 ·641	·798 ·794	0·158 0·153	0·155 (5)
3rd face	·627 ·618 ·633	·794 ·802	0·171 0·177	0·174
4th face	·624 ·619 ·632	·781 ·771	0·159 0·146	0·152 (5)
			Final mean.........	δT = 0·162 sec.

The energy, measured as in the former experiments, was found to be $H_1 = 1{\cdot}6 \times 10^{-5}$ erg/cm. Hence, making the correction for reflections, the theory gives

$$\delta T = 0{\cdot}158 \text{ sec.},$$

a value which is in satisfactory agreement with the above value given by the experiment.

The Effect of Junctions on the Propagation of Electric Waves along Conductors.

By Lord Rayleigh, O.M., F.R.S.

(Received December 2, 1912,—Read January 16, 1913.)

Some interesting problems in electric wave propagation are suggested by an experiment of Hertz.* In its original form waves of the simplest kind travel in the positive direction (fig. 1), outside an infinitely thin conducting cylindrical shell, AA, which comes to an end, say, at the plane $z = 0$. Co-axial with the cylinder a rod or wire BB (of less diameter) extends to infinity in both directions. The conductors being supposed perfect, it is required to determine the waves propagated onwards beyond the cylinder on the positive side of z, as well as those reflected back outside the cylinder and in the annular space between the cylinder and the rod.

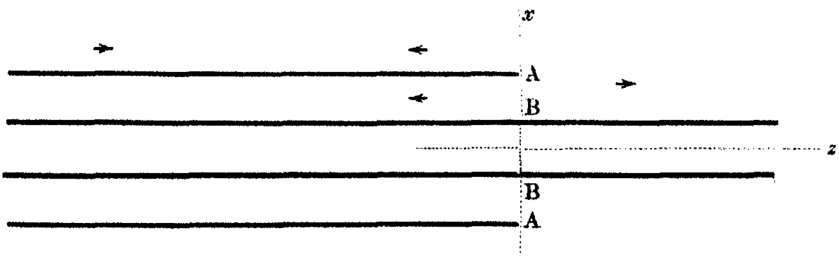


Fig. 1.

So stated, the problem, even if mathematically definite, is probably intractable; but if we modify it by introducing an external co-axial conducting sheath CC (fig. 2), extending to infinity in both directions, and if we further suppose that the diameter of this sheath is small in comparison with the wave-length (λ) of the vibrations, we shall bring it within the scope of approximate methods. It is under this limitation that I propose here to consider the present and a few analogous problems. Some considerations of a more general character are prefixed.

If P, Q, R, be components of electromotive intensity, a, b, c, those of magnetisation, Maxwell's general circuital relations† for the dielectric give

$$\frac{da}{dt} = \frac{dQ}{dz} - \frac{dR}{dy}, \tag{1}$$

* "Ueber die Fortleitung electrischer Wellen durch Drähte," 'Wied. Ann.,' 1889, vol. 37, p. 395.

† 'Phil. Trans.,' 1868; 'Maxwell's Scientific Papers,' vol. 2, p. 128.

and two similar equations, and

$$\frac{dP}{dt} = V^2\left(\frac{dc}{dy} - \frac{db}{dz}\right), \tag{2}$$

also with two similar equations, V being the velocity of propagation. From (1) and (2) we may derive

$$\frac{da}{dx}+\frac{db}{dy}+\frac{dc}{dz} = 0, \qquad \frac{dP}{dx}+\frac{dQ}{dy}+\frac{dR}{dz} = 0\,; \tag{3}$$

and, further, that

$$\left(\frac{d^2}{dt^2} - V^2\nabla^2\right)(P, Q, R, a, b, c) = 0, \tag{4}$$

where

$$\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2. \tag{5}$$

At any point upon the surface of a conductor, regarded as perfect, the condition to be satisfied is that the vector (P, Q, R) be there *normal*. In what follows we shall have to deal only with simple vibrations in which all the quantities are proportional to e^{ipt}, so that d/dt may be replaced by ip.

It may be convenient to commence with some cases where the waves are in two dimensions (x, z) only, supposing that a, c, Q, vanish, while b, P, R, are independent of y. From (1) and (2) we have

$$P\frac{db}{dx} + R\frac{db}{dz} = 0.$$

At the surface of a conductor P, Q, are proportional to the direction cosines of the normal (n); so that the surface condition may be expressed simply by

$$\frac{db}{dn} = 0, \tag{6}$$

which, with

$$\left(\frac{d^2}{dx^2}+\frac{d^2}{dz^2}+k^2\right)b = 0, \tag{7}$$

suffices to determine b. In (7) $k = p/V$. It will be seen that equations (6), (7) are identical with those which apply in two dimensions to aërial vibrations executed in spaces bounded by fixed walls, b then denoting velocity-potential. When b is known, the remaining functions follow at once.

It may be remarked by the way that the above analogy throws light upon the question under what circumstances electric waves are *guided* by conductors. Some high authorities, it would seem, regard such guidance as ensuing in all cases as a consequence of the boundary condition fixing the direction of the electric force. But in Acoustics, though a similar condition holds good, there is no guidance of aërial waves round convex surfaces, and it follows that there is none in the two-dimensional electric vibrations under consideration. Near the *concave* surface of walls there is in both cases

a whispering gallery effect.* The peculiar guidance of electric waves by wires depends upon the conductor being encircled by the magnetic force. No such circulation, for example, could ensue from the incidence of plane waves upon a wire which lies entirely in the plane containing the direction of propagation and that of the magnetic force.

Our first special application is to the extreme form of Hertz's problem (as modified) which occurs when all the radii of the cylindrical surfaces concerned become infinite, while the *differences* CA, AB remain finite and indeed small in comparison with λ. In fig. 2, A, B, C then represent

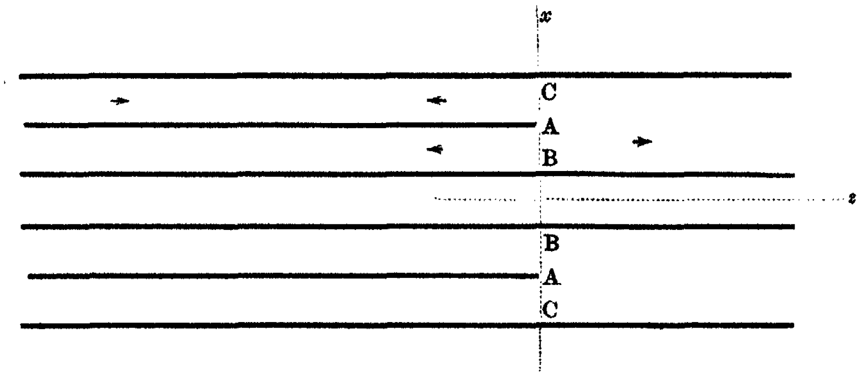


FIG. 2.

planes perpendicular to the plane of the paper and the problem is in two dimensions. The two halves, corresponding to *plus* and *minus* values of x, are isolated, and we need only consider one of them. Availing ourselves of the acoustical analogy, we may at once transfer the solution given (after Poisson) in 'Theory of Sound,' § 264. If the incident wave in CA be represented by f_{CA} and that therein reflected by F, while the waves propagated along CB, AB be denoted by f_{CB}, f_{AB}, we have

$$f'_{CB} = f'_{AB} = \frac{2\,CA}{CB+AB+CA} f'_{CA} = \frac{CA}{CB} f'_{CA} \tag{8}$$

and

$$F' = \frac{AB}{CB} f'_{CA}. \tag{9}$$

The wave in AB is to be regarded as propagated onwards round the corner at A rather than as reflected. As was to be anticipated, the reflected wave F′ is smaller, the smaller is AB. It will be understood that the validity of these results depends upon the assumption that the region round A through which the waves are irregular has dimensions which are negligible in comparison with λ.

* 'Phil. Mag.,' 1910, vol. 20, p. 1001; 'Scientific Papers,' vol. 5, p. 617.

An even simpler example is sketched in fig. 3, where for the present the

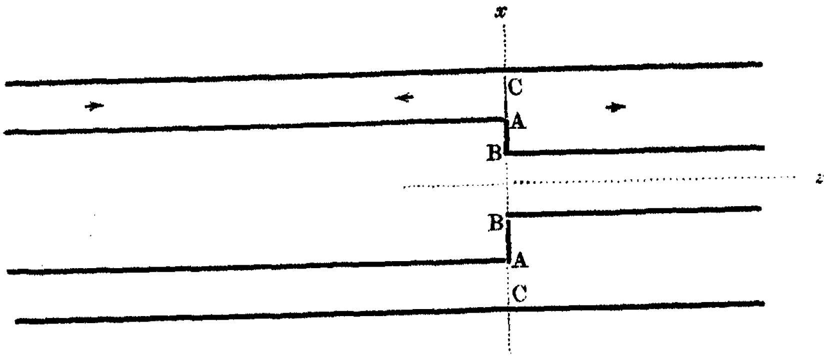


FIG. 3.

various lines represent planes or cylindrical surfaces perpendicular to the paper. One bounding plane C is unbroken. The other boundary consists mainly of two planes with a transition at AB, which, however, may be of any form so long as it is effected within a distance much less than λ. With a notation similar to that used before, f_{CA} may denote the incident positive wave and F the reflected wave, while that propagated onwards in CB is f_{CB}. We obtain in like manner

$$f'_{CB} = \frac{2CA}{CB+CA} f'_{CA}, \tag{10}$$

$$F' = \frac{AB}{CB+CA} f'_{CA}. \tag{11}$$

When AB vanishes we have, of course, $f'_{CB} = f'_{CA}$, $F' = 0$. A little later we shall consider the problem of fig. 3 when the various surfaces are of revolution round the axis of z.

Leaving the two-dimensional examples, we find that the same general method is applicable, always under the condition that the region occupied by irregular waves has dimensions which are small in comparison with λ. Within this region a simplified form of the general equations avails, and thus the difficulty is turned.

An increase in λ means a decrease in p. When this goes far enough, it justifies the omission of d/dt in equations (1), (2), (3), (4). Thus P, Q, R become the derivatives of a simple potential function ϕ, which itself satisfies $\nabla^2\phi = 0$; that is, the electric forces obey the laws of electrostatics. Similarly a, b, c are derivatives of another function ψ satisfying the same equation. The only difference is that ψ may be multivalued. The magnetism is that due to steady electric currents. If several wires meet in a point, the total current is zero. This expresses itself in terms

of a, b, c as a relation between the "circulations." The method then consists in forming the solutions which apply to the parts at a distance on the two sides from the region of irregularity, and in accommodating them to one another by the conditions which hold good at the margins of this region in virtue of the fact that it is small.

In the application to the problem of fig. 3 we will suppose that the conductors are of revolution round z, though this limitation is not really imposed by the method itself. The problem of the regular waves (whatever may be form of section) was considered in a former paper.* All the dependent variables expressing the electric conditions being proportional to $e^{i(pt \pm kz)}$, d^2/dt^2 in (4) compensates $V^2 d^2/dz^2$, so that

$$\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)(P, Q, R, a, b, c) = 0; \tag{12}$$

also R and c vanish. In the present case we have for the negative side, where there is both a direct and a reflected wave,

$$P, Q, R = e^{ipt}(H_1 e^{-ikz} + K_1 e^{ikz})\left(\frac{d}{dx}, \frac{d}{dy}, 0\right)\log r, \tag{13}$$

where r is the distance of any point from the axis of symmetry, and H_1, K_1 are arbitrary constants. Corresponding to (13),

$$V(a, b, c) = e^{ipt}(-H_1 e^{-ikz} + K_1 e^{ikz})\left(\frac{d}{dy}, -\frac{d}{dx}, 0\right)\log r. \tag{14}$$

In the region of regular waves on the positive side there is supposed to be no wave propagated in the negative direction. Here accordingly

$$P, Q, R = H_2 e^{i(pt-kz)}\left(\frac{d}{dx}, \frac{d}{dy}, 0\right)\log r, \tag{15}$$

$$V(a, b, c) = H_2 e^{i(pt-kz)}\left(-\frac{d}{dy}, \frac{d}{dx}, 0\right)\log r, \tag{16}$$

H_2 being another constant. We have now to determine the relations between the constants H_1, K_1, H_2, hitherto arbitrary, in terms of the remaining data.

For this purpose consider cross-sections on the two sides both near the origin and yet within the regions of regular waves. The electric force as expressed in (13), (15) is purely radial. On the positive side its integral between r_2 the radius of the inner and r' that of the outer conductor is, with omission of e^{ipt},

$$H_2 e^{-ikz}\log(r'/r_2),$$

z having the value proper to the section. On the negative side the corresponding integral is

$$(H_1 e^{-ikz} + K_1 e^{ikz})\log(r'/r_1),$$

* 'Phil. Mag.,' 1897, vol. 44, p. 199; 'Scientific Papers,' vol. 4, p. 327.

r_1 being the radius of the inner conductor at that place. But when we consider the intermediate region, where electrostatical laws prevail, we recognise that these two integrals must be equal; and further that the exponentials may be identified with unity. Accordingly, the first relation is

$$(H_1+K_1)\log(r'/r_1) = H_2\log(r'/r_2). \tag{17}$$

In like manner the magnetic force in (14), (16) is purely circumferential. And the circulations at the two sections are as H_1-K_1 and H_2. But since these circulations, representing electric currents which may be treated as steady, are equal, we have as the second relation—

$$H_1-K_1 = H_2. \tag{18}$$

The two relations (17), (18) give the wave propagated onwards H_2 and that reflected K_1 in terms of the incident wave H_1. If $r_2 = r_1$, we have of course, $H_2 = H_1$, $K_1 = 0$.

If we suppose r_1, r_2, r' all great and nearly equal and expand the logarithms, we fall back on the solution for the two-dimensional case already given.

In the above the radius of the outer sheath is supposed uniform throughout. If in the neighbourhood of the origin the radius of the sheath changes from r_1' to r_2', while (as before) that of the inner conductor changes from r_1 to r_2, we have instead of (17),

$$(H_1+K_1)\log(r_1'/r_1) = H_2\log(r_2'/r_2), \tag{19}$$

while (18) remains undisturbed.

In (19) the logarithmic functions are proportional to the reciprocals of the electric capacities of the system on the two sides, reckoned in each case per unit of length. From the general theory given in the paper referred to we may infer that this substitution suffices to liberate us from the restriction to symmetry round the axis hitherto imposed. The more general functions which then replace $\log r$ on the two sides must be chosen with such coefficients as will make the circulations of magnetic force equal. The generalisation here indicated applies equally in the other problems of this paper.

In Hertz's problem, fig. 2, the method is similar. In the region of regular waves on the left in CA we may retain (13), (14), and for the regular waves on the right in CB we retain (15), (16). But now in addition for the regular waves on the left in AB, we have

$$P, Q, R = K_3 e^{i(pt+kz)}\left(\frac{d}{dx}, \frac{d}{dy}, 0\right)\log r, \tag{20}$$

$$V(a, b, c) = K_3 e^{i(pt+kz)}\left(\frac{d}{dy}, -\frac{d}{dx}, 0\right)\log r. \tag{21}$$

Three conditions are now required to determine K_1, H_2, K_3 in terms of H_1. We shall denote the radii taken in order, viz., $\frac{1}{2}$BB, $\frac{1}{2}$AA, $\frac{1}{2}$CC, by r_1, r_2, r_3 respectively. As in (17), the electric forces give

$$(H_1+K_1)\log\frac{r_3}{r_2}+K_3\log\frac{r_2}{r_1} = H_2\log\frac{r_3}{r_1}. \tag{22}$$

The magnetic forces yield two equations, which may be regarded as expressing that the currents are the same on the two sides along BB, and that, since the section is at a negligible distance from the insulated end, there is no current in AA. Thus

$$H_1-K_1 = -K_3 = H_2. \tag{23}$$

From (22) and (23)

$$\frac{K_1}{H_1} = \frac{\log r_2-\log r_1}{\log r_3-\log r_1}, \tag{24}$$

$$H_2 = -K_3 = \frac{\log r_3-\log r_2}{\log r_3-\log r_1}. \tag{25}$$

If r_2 exceeds r_1 but little, K_1 tends to vanish, while H_2 and $-K_3$ approach unity. Again, if the radii are all great, (24), (25) reduce to

$$\frac{K_1}{H_1} = \frac{r_2-r_1}{r_3-r_1}, \quad H_2 = -K_3 = \frac{r_3-r_2}{r_3-r_1}, \tag{26}$$

as already found in (8), (9).

The same method applies with but little variation to the more general problem where waves between one wire and sheath (r_1, r_1') divide so as to pass along several wires and sheaths (r_2, r_2'), (r_3, r_3'), etc., always under the condition that the whole region of irregularity is negligible in comparison with the wave-length.* The various wires and sheaths are, of course, supposed to be continuous. With a similar notation the direct and reflected waves along the first wire are denoted by H_1, K_1, and those propagated onwards along the second, third, and other wires by H_2, H_3, etc. The equations are—

$$(H_1+K_1)\log\frac{r_1'}{r_1} = H_2\log\frac{r_2'}{r_2} = H_3\log\frac{r_3'}{r_3} = \ldots\ldots, \tag{27}$$

$$H_1-K_1 = H_2 = H_3 = \ldots\ldots.$$

It is hardly necessary to detail obvious particular cases.

The success of the method used in these problems depends upon the assumption of a great wave-length. This, of course, constitutes a limitation, but it has the advantage of eliminating the irregular motion at the junctions.

* This condition will usually suffice. But extreme cases may be proposed where, in spite of the smallness of the intermediate region, its shape is such as to entail natural resonances of frequency agreeing with that of the principal waves. The method would then fail.

In the two-dimensional examples it might be possible to pursue the approximation by determining the character of the irregular waves, at least to a certain extent, somewhat as in the question of the correction for the open end of an organ pipe.

Duration of Luminosity of Electric Discharge in Gases and Vapours.

By the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received December 19, 1912,—Read January 16, 1913.)

§ 1. *Introduction.*

The electric discharge produces luminosity in any gas or vapour through which it passes. The question presents itself, Does the luminosity persist after the current has ceased, or does it stop immediately? A full answer is likely to be of great importance in unravelling the cause and mechanism of the luminosity. There are existing observations bearing on the subject, but these are somewhat scattered in the literature, and, so far as I am aware, their mutual relations have not been pointed out. It is hoped in this paper to do something towards systematising and extending them.

The most conspicuous phenomena in this connection are the various forms of afterglow which have been discussed in previous papers.* But these are not really relevant to the present subject, for they are due to secondary causes of a chemical nature. Some of them, produced in gaseous mixtures containing oxygen, are due to the interaction of ozone with other substances present. Others, again, are connected with the formation of an active modification of nitrogen. In none of these cases can the after-luminosity be considered continuous with the luminosity of the discharge which produced it. For it is always much less brilliant, even at first, and always has a quite different spectrum.

Several experimenters have found, by examining the leyden jar spark with a rotating mirror, that its luminosity may persist much longer than the

* 'Phys. Soc. Proc.,' 1910, vol. 23, pp. 66, 147; 1911, vol. 24, p. 1; 'Roy. Soc. Proc.,' 1911, A, vol. 85, pp. 219, 377, 533; 1912, vol. 86, pp. 56, 105, 262, 529; 1912, vol. 87, pp. 179, 302.

electric current which gave rise to the luminosity.* This effect is observed when the electrodes are formed of a metal more or less easy of volatilisation. If a non-volatile metal like platinum is used, the spark current passes only through air, and no persistence of luminosity is observed. For this reason such sparks are suitable as a source of light for the photography of flying bullets.

So far I have referred to the case of negligible inductance in the spark circuit. If the inductance is considerable, the (alternating) current is, of course, prolonged thereby. In this case new streams of luminous vapour come off from the volatile electrodes at each oscillation, and add their effect to that of the luminous vapour already accumulated there. These are the "streamers." The term is conveniently extended to the case of an almost non-inductive circuit. Here there are, of course, still a number of streamers; but they cannot be separated at any practicable speed of the mirror, and therefore appear to form one single stream of luminous vapour from each electrode.

The streamers, and the persistence of luminosity, can also be shown by a method due to Hemsalech.† He uses a coil with an iron core; the hysteresis losses in the core reduce the spark to one single oscillation; and the duration of the luminosity is observed by blowing the luminous vapour away by a rapid current of air. The luminous track can be followed for an appreciable distance, and spectroscopic observations show which lines last longest.

The connection of the streamers with another known phenomenon does not seem to have been explicitly pointed out. This is the so-called "aureole" of the mercury vapour lamp.‡ If an arc discharge is passed between mercury electrodes in an exhausted vessel, intense luminosity is produced, and enough heat developed to raise considerable vapour pressure over the mercury electrodes. If provision is made for allowing the mercury vapour to distil away into a cooled receiver, the moving stream of vapour is found to carry its luminosity with it. The intensity diminishes as the vapour gets further from the lamp, owing to the lapse of time during its journey; but it is important to notice that there is perfect continuity in intensity from the

* Boys, 'Nature,' vol. 47, p. 416, 1893; Schuster and Hemsalech, 'Phil. Trans.,' 1900, A, vol. 193, p. 189; Schenck, 'Astrophys. Journ.,' 1901, vol. 14, p. 116; Milner, 'Phil. Trans.,' 1909, A, vol. 209, p. 71.

† 'Comptes Rendus,' 1910, vol. 150, p. 1743; 1910, vol. 151, p. 220.

‡ Stark and Reich, 'Phys. Zeit.,' 1903, vol. 4, p. 324; Stark, 'Phys. Zeit.,' 1903, vol. 4, p. 440; Stark, 'Ann. d. Phys.,' 1904, vol. 14, p. 522; Stark, Retschinsky, and Schnaposnikoff, 'Ann. d. Phys.,' 1905, vol. 18, p. 231; W. Matthies, 1910, 'Verh. d. Deut. Phys. Gesell.,' 1910, vol. 12, p. 754.

point where it leaves the lamp until it is completely extinguished.* Immediately after it has left the region where the arc is passing, it is not appreciably less luminous than in the arc. How far the luminosity will travel depends on the size of the tube, and the resulting velocity of flow. Under favourable conditions, the luminosity may be made to travel 50 cm., or even more. If the channel is anywhere less than about 3 mm. diameter, the luminosity hardly travels any appreciable distance from the arc.

The mass of mercury distilled in a few minutes amounts to several grammes, and consequently the linear velocity of the rarefied vapour must be very great It is estimated by Stark as of the order of 3×10^4 cm. per second.

This method of observing the duration of the luminosity is much more advantageous than the preceding, where it can be applied. Great practical difficulties stand in the way of applying it to cases other than mercury, though they may, perhaps, be overcome in some instances.

§ 2. *New Method of Observing the Streamers.*

The principle is as follows: The electrodes are wires of the metal under investigation, *aa*, *bb*, fig. 1. They are inserted into the opposite ends of a

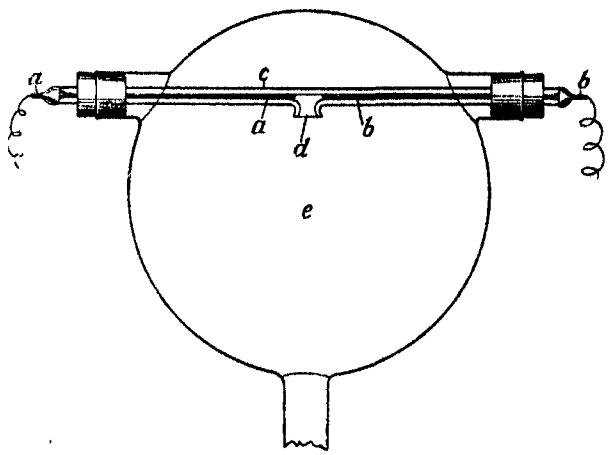


FIG. 1.

glass tube *c* of 1·5 or 2 mm. internal diameter (Sprengel tubing) so that the ends are about 5 mm. apart. A hole *d* is blown in the side of the tube, between the ends of the wire, and when the jar spark passes, the metallic vapour formed is blown out of this hole, and out of the region of electric force between the electrodes. The volume of vapour formed is not enough

* Under some experimental conditions there are alternations of light and darkness. These are due, as Matthies has pointed out, to alternations of higher and lower pressure produced by hydrodynamical causes.

to distinctly exude from the hole at atmospheric pressure; but the tube is arranged inside a receiver *e* which can be exhausted, and the effect becomes conspicuous at a pressure of a few millimetres of mercury. The vapour is shot out of the side hole in a distinct jet several millimetres in length, visible by its own luminosity, which is seen to be continuous with that of the spark. The jar is charged by an induction coil and an air gap is used in series with the apparatus of fig. 1. When the metal is difficult to obtain in the form of wire, iron wires may be used, and a fragment of the volatile metal under investigation introduced into the gap, and in contact with the end of one wire. The same method is applicable to non-metals, such as sulphur and iodine. The apparatus must be placed with *d* upwards in this case.

At pressures of a few millimetres of mercury the luminous jet is of small volume, the vapour making its way out in a comparatively narrow and sharply defined stream. The outlines of the mass of luminous vapour are curiously hard, and not infrequently ragged and irregular.

Under these conditions, the residual air in the spark gap is driven out along with the metallic vapour, and gives the characteristic greenish-yellow afterglow, due to the reaction of ozone with nitric oxide. This luminosity is far more persistent than that due to the metal, and is perceptible right across the vessel, as a prolongation of the stream of metallic vapour. The metallic glow is much the more brilliant, during the short time for which it lasts. In fig. 2 the shading *a* represents the luminous metallic

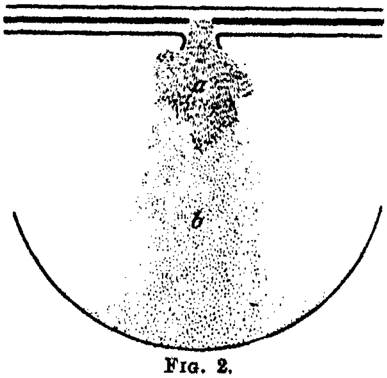


FIG. 2.

vapour, *b* the greenish-yellow afterglow, which flattens itself out against the glass wall, as shown.

As the air pressure is reduced the greenish-yellow afterglow just mentioned disappears, and the metallic glow spreads out and becomes more diffuse. At moderate vacua, say 1 mm. or less pressure, it issues almost

equally over a wide angle from the aperture; and its outline is rounded (fig. 3).* At high vacua the vapour may expand enough to fill nearly the whole of a 300 c.c. flask: but in this case the luminosity is diluted to extreme faintness.

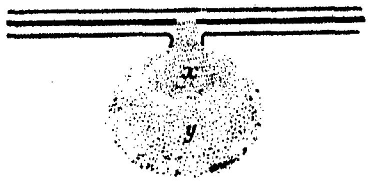


FIG. 3.

At these low pressures it is difficult or impossible to prevent stray electrical discharges through the outer vessel, of the kind called (not very correctly) electrostatic. These give rise to a faint luminosity of their own, particularly in the connecting tubes leading to the pump. It is certain, however, that the metallic glows described are not connected with this, since there are no stray discharges when air is present to a pressure of a few millimetres; and the phenomena can be traced continuously from that stage.

§ 3. *Effects with Vapours of Various Elements.*

The vapours investigated all gave line spectra exclusively:—

Sodium.—Bright yellow glow. Could be made to fill large volume.

Thallium.—Bright green glow. Conspicuous.

Calcium.—Good orange glow.

Zinc and *Cadmium.*—Well developed, greenish glows.

Mercury.—Amalgamated copper electrodes were used, which, however, only carried enough mercury for a short time. Glow much more brilliant and voluminous than in most other cases, on account of the brilliancy of the mercury discharge and the volatility of the metal. Colour, greenish.

Arsenic.—Dull yellow glow, not very striking. Glass soon obscured by the deposited metal.

Magnesium.—An interesting effect was observed in this case. As the surrounding air was removed, the glow which first emerged was bright green. As, however, the pressure diminished, a blue glow was seen at the base of the luminous cloud (see fig. 3), where x is the blue portion, surrounded by the outer green envelope y. The glow at this stage was focussed on the slit of a spectroscope, and it was seen that the luminosity of the blue line 4481 from the side hole extended a short distance only, while the green

* The significance of the shading is *not* the same in fig. 3 as in fig. 2. For explanation of the different shading of the inner part of the mass of metallic vapour in fig. 3 see below.

triplet 5172 extended two or three times as far. The former line is characteristic of the spark discharge only; the latter appears in the arc as well.

Lead.—A similar effect is noticed in this case. The light which first issues from the side hole is blue; this expands to the usual rounded form (fig. 3) as the air is removed, and eventually an inner zone of greyish light (x, fig. 3) emerges very clearly distinct from the outer reddish blue one (y, fig. 3). The spectrum of this glow was photographed, and, as before, the spark lines were confined to the inner zone, while the arc lines extended right through to the limits of the outer one. The principal spark lines photographed were 4386 and 4246, while the chief arc lines were 4062, 3740, 3683, and 3572.

These results for magnesium and lead confirm the conclusions obtained by Milner.* Using a revolving mirror to draw out the spectrum of the spark, he found that the arc lines were much the most persistent. Probably a closer spectroscopic scrutiny of the various glows I obtained would show other instances. In the particular cases cited, the difference is conspicuous by direct colour observation, without the spectroscope.

Selenium gave a fine, well-developed glow, filling a great part of the outer vessel with brilliant luminosity. The red deposit of sublimed selenium on the glass soon hindered observation, and made it necessary to clean the outer vessel.

Sulphur gave an extensive blue glow, showing, like selenium, the line spectrum. It is clear that phenomena of this class are not confined to the metals, as I was at one time disposed to think.

Phosphorus also gave a glow.

Iodine gave a not very extended glow. The colour of the spark itself was green. Many of the lines in this green light did not penetrate any appreciable distance out, and the glow due to the remainder had a buff colour, with a blue outer fringe. There is room for a more detailed investigation of this and the other halogens in connection with their general spectroscopy.

§ 4. *Effects with the Common Gases.*

Substantially the same method is applicable in this case. The discharge tube may have an internal diameter of 5 mm., and the electrodes may be 1 cm. apart. The latter may be of iron, which does not volatilise appreciably under the conditions. They should be large enough to fill the entire diameter of the tube. The gas, heated by the discharge, will not then have any means of escape, except through the lateral hole. It is forced out, and shows luminosity, as do the metallic vapours.

* 'Phil. Trans.,' 1909, A, vol. 209, p. 77.

Since it is necessary to have an appreciable quantity of the gas in the region between the electrodes, we cannot reduce the gas pressure in the surrounding vessel very low, as was possible when experimenting with the vapours of solids. Such vapours are formed inside the inner discharge vessel when the spark passes. The gases, on the other hand, must be present in the inner vessel to begin with, and therefore necessarily in the outer one too, which is in communication with it. For this reason no great expansion of the exuded glow can be obtained in the outer vessel.

Partly on this account, but much more, I believe, owing to the inherently short life of their luminosity, the exuded glow obtained with the permanent gases is a comparatively inconspicuous effect. I have never got the glow to travel out more than about 5 mm. from the orifice.

Hydrogen shows the effect best. The most suitable pressure with this, as with the other gases, is about 1 cm. of mercury, at least, with the above dimensions of apparatus. The luminosity is fiery red (due mainly to H_α) and not much less brilliant than the spark itself. It dies out very abruptly. Under some conditions it is succeeded by the blue afterglow of Hertz, after the fashion of fig. 2. The latter I have shown to be connected with a sulphur impurity.*

Nitrogen or *air* do not show the effect at all conspicuously. The luminosity scarcely exudes perceptibly from the orifice, presumably owing to its very short duration. What there is of it shows the nitrogen line spectrum. When pure nitrogen is used, the glow of long duration, due to active nitrogen, may sometimes be seen extending right across the vessel. But this is not very conspicuous, for, as shown previously,† a discharge giving only the line spectrum does not excite it.‡

Oxygen gives the effect almost as well as hydrogen. The exuded glow shows the line spectrum.

Carbon dioxide also shows the duration of its luminosity by the exuded glow. This gives a band spectrum identical with that of the discharge—the only band spectrum observed in these experiments.

§ 5. *Summary.*

The luminosity of the electric discharge appreciably survives the current not only in metallic vapours but also in the vapours of non-metals, and in the permanent gases. The luminosity fades away in a continuous manner,

* See 'Proc. Roy. Soc.,' 1912, A, vol. 86, p. 529.

† Fowler and Strutt, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 385.

‡ Presumably some trace of the band spectrum is present in these experiments, or it would not be excited at all.

and without immediate change of spectrum, when the current ceases. Sometimes, however, a change of spectrum eventually results from unequal decay of the lines.

These effects, which last less than 1/1000 of a second, are distinct, not only in degree, but in kind from the afterglows in nitrogen, in gaseous mixtures containing oxygen, and in gaseous mixtures containing hydrogen, previously investigated. These have durations extending in some cases to several minutes, and their spectra are from the first radically different from those of the exciting discharges. As previously shown, they are due to secondary chemical actions of substances produced by the discharge.

The Positive Ionisation Produced by Platinum and by Certain Salts when Heated.

By Frank Horton, M.A., D.Sc., Fellow of St. John's College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received November 28, 1912,—Read January 16, 1913.)

In the 'Proceedings of the Royal Society' for 1910,* there is an account of a spectroscopic investigation of the nature of the carriers of positive electricity when an electric current is sent from a glowing platinum strip covered with aluminium phosphate to a surrounding platinum electrode, the whole being contained in a highly evacuated vessel. It was found that aluminium phosphate heated under these conditions evolved carbon monoxide gas, and as a molecule of this gas carrying a single electronic charge gives a value for e/m which agrees fairly well with the mean value found for the carriers of positive electricity from heated metals, it was concluded that the positive ions are charged molecules of carbon monoxide. Hydrogen was also detected in the gas evolved by the hot electrode in this experiment, and it now seems probable that atoms of hydrogen also take part in carrying the current, for Garrett has found that about 10 per cent. of the positive ions present when aluminium phosphate is heated on a platinum strip in a vacuum have a mass corresponding to that of the hydrogen atom.†

A different view of the nature of the positive ions from glowing metals and metallic salts is held by Prof. O. W. Richardson. As the result of

* Series A, vol. 84, p. 433.

† A. E. Garrett, 'Phil. Mag.,' 1910, VI, vol. 20, p. 582.

numerous experiments by himself and his pupils,* Richardson has come to the conclusion that the positive ions emitted by heated salts are charged atoms of the metallic constituent of the salt under test, and that in the case of incandescent metals the carriers of positive electricity are charged atoms of sodium or potassium which are present as impurities in the form of salts. It was in order to obtain further evidence of the origin of the positive ionisation from incandescent bodies that the experiments described in the present paper were undertaken. The paper contains the results of an investigation of the effect of the surrounding gas upon the thermionic currents from different substances. The general method of experiment was as follows:—The positive leak from a strip of platinum foil was first carefully investigated. Observations were made of its rate of decay with time, of its variation with the potential difference used, and with the gas pressure in the apparatus. The strip was then covered with the salt to be tested, and the observations were repeated. When the experiments with this salt were complete, the strip of platinum was carefully cleaned and another salt substituted. In this way observations were made of the thermionic emissions under exactly similar conditions from platinum, from four samples of aluminium phosphate, from two samples of sodium ortho-phosphate, and from one sample of sodium pyro-phosphate. Comparisons were made, in particular, at the two temperatures 1080° and 1190° C. In an earlier paper,† in which the discharge of positive electricity from sodium phosphate heated in different gases was examined, 800° C. was used as the temperature of comparison, and reasons were given why it is best to work at as low a temperature as possible. In the present experiments, however, it was found in some cases that even at 1080° C. the thermionic current became so small on long-continued heating as to be hardly measurable with the galvanometer used, and it was on this account that the comparisons were finally made at 1190° C. These earlier experiments with phosphates of sodium† and lithium‡ have shown that the nature of the surrounding gas has a considerable effect on the magnitude of the thermionic current. In the present experiments the gas in the apparatus was usually air, but in one instance, with a sample of pure aluminium phosphate, some experiments were made in carbon monoxide. The positive leak in this gas was found to be larger than that under the same conditions in air, but in other respects

* O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 1; 'Phil. Mag.,' 1908, VI, vol. 16, p. 740; O. W. Richardson and E. R. Hulbirt, 'Phil. Mag.,' 1910, VI, vol. 20, p. 545; O. W. Richardson, 'Phil. Mag.,' 1910, VI, vol. 20, p. 981; 'Phil. Mag.,' 1911, VI, vol. 22, p. 669; C. J. Davisson, 'Phil. Mag.,' 1912, VI, vol. 23, p. 121.

† 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 89.

‡ 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 318.

similar results were obtained with the two gases. It was therefore thought undesirable to prolong the research by repeating experiments with different gases in the case of the other substances. A description of the apparatus used and an account of the results obtained will now be given.

Description of the Apparatus.

The discharge tube used in these experiments is represented in fig. 1. It is made of glass, and consists of two parts which fit together by a ground joint with a mercury seal. The platinum strip A can thus easily be removed for covering with the salt to be experimented on. When in position it is situated vertically in the centre of the tube between two parallel platinum plates P, P, which together form the negative electrode. The strip A is of thin foil 2 cm. long and 2 mm. wide. It can be heated electrically by means of the thick platinum leads B and C, the current being supplied from eight accumulator cells, and regulated by wire resistances. The temperature of the central portion of the strip is obtained by a thermo-couple consisting of two fine wires, one of pure platinum and the other of platinum with 10 per cent. of rhodium. These wires are 0·0025 cm. in diameter, and are fused together at one end, the junction being lightly welded on to the centre of one side of the platinum strip as indicated in the diagram. The wires are insulated for the greater part of their length by fine glass tubes, and are sealed through the lower portion of the discharge tube at E. The thermo-electric current is measured by a d'Arsonval galvanometer, and the deflections are standardised from observations of the melting point of pure potassium sulphate, making use of the curve given by Callendar* for this purpose. The welding of the thermo-junction on to the platinum strip is an operation requiring great care. A very small junction has to be made, and this must be welded to the strip

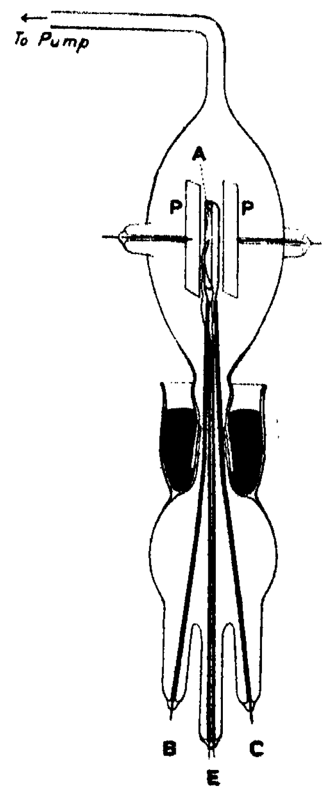


FIG. 1.

A, platinum strip forming the anode; B, C, leads of heating circuit; E, wires of thermo-couple; P, P, platinum plates forming the cathode.

* Callendar, 'Phil. Mag.,' vol. 48, p. 519.

without any part of the fine wires becoming affixed, otherwise they may tap off a portion of the E.M.F. of the heating circuit and thus invalidate the temperature observations. Before standardising the thermo-couple used in these experiments, it was ascertained that the galvanometer used to indicate the temperature gave the same deflection when the direction of the heating current was reversed.

The two platinum plates P, P, are made of stout metal, and are 2·5 cm. long by 1 cm. wide. They are connected together by a wire outside the discharge tube. The plates were about 1 cm. apart, and were at equal distances from the anode A. The thick platinum wires B and C of the heating circuit were covered with glass in order to make them more rigid and to keep them cool. The whole apparatus was very carefully cleaned out with hot chromic acid and with boiling nitric acid, and then washed with distilled water and dried before being fixed on to the mercury pump. A drying tube with phosphorus pentoxide was between the discharge tube and the pump, and the latter was also connected to a McLeod gauge for registering the gas pressure. In order to facilitate the gradual alteration of the pressure in the apparatus, there was in connection with it a large vertical glass tube 5 cm. wide and 50 cm. long, which could be filled with mercury by raising a cistern of mercury attached by indiarubber tubing to its lower end. For obtaining a thermionic current the platinum strip A was connected to the positive pole of a set of small accumulator cells. The platinum plates P were connected to the negative pole of the battery through a fine tinfoil fuse and a sensitive d'Arsonval galvanometer. The galvanometer was well insulated on paraffin blocks; it gave a deflection of one scale division for a current of $3{\cdot}68 \times 10^{-10}$ ampère, and could be shunted for measuring larger currents.

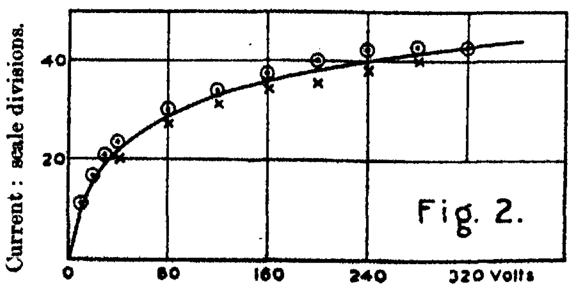
The Experiments with Platinum.

Before being finally fitted up for experimenting, the platinum strip was boiled in strong nitric acid and then carefully washed with hot water. The first observation of the thermionic current was made with a potential difference of 40 volts, and an air pressure of 3·42 mm. in the apparatus. As the temperature of the platinum strip was gradually raised a current was first detected at 700° C.; at higher temperatures the current was larger, but it decreased very rapidly with time in the manner which has already been described by Richardson.* A comparison of the rates of decay of the positive emission from platinum, and from the salts experimented on, will be given in a later part of this paper, but it will be convenient to point out here that

* O. W. Richardson, 'Phil. Mag.,' 1903, VI, vol. 6, p. 80.

although the current under given conditions of voltage and gas pressure became roughly constant after about five or six hours' heating, it continued to decrease slowly throughout the series of experiments with the platinum anode, and if the heating had been continued for some hours longer I believe the positive leak would have been too small to measure on the galvanometer used. It should also be mentioned that after leaving the platinum strip cold overnight, a much larger current was obtained when first testing on the following morning. This effect was most noticeable when the gas pressure in the apparatus was very low, and I thought it was possibly due to phosphorus vapour coming over from the phophorus pentoxide drying tube, for commercial phosphorus pentoxide often contains free phosphorus. I investigated this point by having a mercury barometer tube so arranged that by raising the cistern I could cut off the connection between the discharge tube and the rest of the apparatus. Doing this, I found that the largely increased leak was still obtained on allowing the strip to remain cold for several hours, although there was no possibility of it having come in contact with phosphorus vapour. This effect is exactly similar to that which was obtained when investigating the negative leak from platinum at higher temperatures,* and I believe it is due to the mercury vapour from the pump forming some compound with the platinum. The abnormally high value of the thermionic current only lasted for a short time; in a few minutes the leak had decreased to a steady value, usually somewhat smaller than it had on the previous evening. This decrease in the leak was accompanied by a slight increase in the electrical resistance of the strip, which suggests that some volatile product was subliming from its surface. Even at the highest temperature of these experiments no negative leak could be detected while this process was going on.

When the thermionic current had been reduced to its nearly constant value, a series of observations of the relation between the current and the applied



E.M.F. were made. A typical curve showing this relation is given in fig. 2. This was obtained with the anode at 1190° C., and with a pressure of 0·01 mm.

* 'Phil. Trans.,' 1907, A, vol. 207, p. 149.

of air in the apparatus. The values of the current obtained when the potential difference was being gradually increased are marked ⊙, and those obtained on decreasing the voltage are marked ×. These fall slightly below the first set—a result which was obtained with each of the anodes used in these experiments. The difference in the two readings is not much in the case of platinum, but when this is covered with aluminium phosphate a larger hysteresis effect is obtained. This will be referred to again when the experiments with aluminium phosphate are being considered. The shape of the curve in fig. 2 is similar to that given by Richardson* for platinum at 976° C. in air at atmospheric pressure. It will be seen that up to 320 volts the current is never completely saturated, but that after about 120 volts it increases approximately proportionally to the voltage. At higher pressures the linear part of the curve did not begin until a somewhat larger E.M.F. was reached, indicating that it was more difficult to saturate the current under these conditions. In my earlier experiments with sodium phosphate, which were performed with an apparatus of similar construction, and of about the same dimensions, as that used in the present research, fairly complete saturation was obtained with 40 volts potential difference, even with a pressure of 2 cm. of air in the discharge tube. This difference is no doubt due to the different temperatures used in the two cases. The sodium phosphate anode in the earlier research was only heated to 800° C., whereas the curve of fig. 2 corresponds to a temperature of 1190° C. In his experiments with platinum, already referred to, Richardson also found that it was more difficult to saturate the current at high temperatures, and he states that this may possibly be due to the relatively greater magnitude of the negative ionisation, which would make recombination a factor to be reckoned with. In the present experiments I could detect no negative emission at 1190° C., and I think the difficulty in saturating the current may be due to the presence of slowly-moving ions at this high temperature. Rutherford,† when measuring the velocity of the positive ions from a sheet of platinum heated electrically in air at atmospheric pressure, found that slowly-moving ions were formed in increasing numbers as the temperature of the platinum was raised. These ions probably owe their origin to the dust which is produced by the disintegration of hot platinum, and may be formed by gas ions sticking to the dust particles.

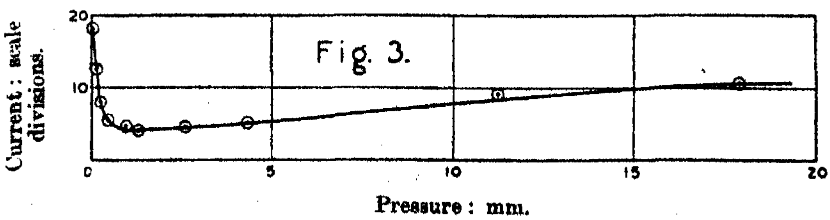
With each of the anodes used in the present apparatus it was found that when the applied potential difference had been raised to 200 volts, the thermionic current was well within the stage when the increase with

* O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 40.

† E. Rutherford, 'Phys. Rev.,' 1901, vol. 13, p. 321.

increasing voltage is small and uniform, and this voltage was used for the purpose of comparing the various thermionic emissions. In the experiments with different gas-pressures in the apparatus, it was found that the form of the current-pressure curve was the same whether a potential difference of 40 volts or of 200 volts was used. This was tested in several cases in order to make quite sure that the applied voltage was not an important factor in the results obtained.

Before the series of observations of the variation of the positive emission from the hot platinum strip with the pressure of the residual air in the apparatus were begun, a test was made to see whether the same value of the current could be obtained if the platinum strip was allowed to cool down for a few minutes, and was then reheated to the original temperature. It was found that after reheating for a few minutes the original steady value of the current was obtained. In taking a series of observations at different pressures it was usual to begin at the highest pressure, and gradually pump the air out of the apparatus. After each observation of the thermionic current, while the pressure was being reduced, the heating current was cut off, and the platinum strip was allowed to cool down. On reheating at the lower pressure, a few minutes were allowed for the current to become steady before the new reading of the galvanometer deflection was taken. By cutting off the heating current during the alteration of pressure one is able to guard against accidentally overheating the anode—a most important precaution, for if the temperature is raised too high, the thermionic current at the lower temperature is at first larger than the normal value, and it takes some time before the steady state is obtained. In this way observations of the thermionic current under different potential differences were made at pressures between about 60 mm. and a good vacuum, the temperature of the anode being in the first experiments 1080° C., and in the later ones 1190° C. It was found that there was very little difference in the magnitude of the current at pressures between 60 mm. and 30 mm. The relation between the current and the pressure at lower pressures will be seen from the curve of fig. 3, which was obtained with the anode at 1190° C., and with a potential difference of 160 volts.



The current decreases steadily with the pressure until a pressure of about 1 mm. is reached, after which there is a sharp increase in the current as the pressure is still further reduced. At pressures below 0·03 mm. the current was always rather irregular, but usually tended to decrease as the pressure was lowered. These irregularities are possibly due to an inaccurate knowledge of the pressure in the discharge tube containing the glowing platinum, which is continually evolving gas. At low pressures this evolution may conceivably cause the gas-pressure in the discharge tube to be much greater than that registered on the McLeod gauge. Another difficulty in making observations at very low pressures is the mercury vapour which comes over from the pump, and which at the ordinary temperature of the laboratory has a pressure of about 0·001 mm.,* so that observations cannot be taken at pressures lower than this unless arrangements are made to prevent mercury vapour from entering the discharge tube. It seems not improbable that the rapid increase in the positive leak with diminishing pressures below about 0·5 mm. is due to chemical action between the mercury vapour and the hot platinum, and it would be interesting to repeat the observations, taking care to exclude mercury from the discharge tube. It should be mentioned that observations of the thermionic current made at gradually increasing pressures gave curves which were similar to the curve of fig. 3.

The Experiments with Aluminium Phosphate.

Sir J. J. Thomson found that aluminium phosphate heated in air at atmospheric pressure gave rise to a much larger emission of positive ions than any other salt of the large number he tested under similar conditions.† In the present research four samples of aluminium phosphate were tested, and for convenience these will be numbered in the order in which they were used. Sample No. II was from the same bottle as that tested by Sir J. J. Thomson; it was the ordinary commercial pure salt. Sample IV was also sold as pure by the chemist from whom it was obtained. The spectroscopic test showed that each of these specimens contained sodium. Richardson holds that the positive emission from commercial aluminium phosphate—which he did not find to be remarkably large—is due to the presence of alkaline impurities. In the 'Philosophical Magazine' for November, 1911, he has described some experiments made with aluminium phosphate prepared from materials all of which had undergone distillation, hoping in this way to obtain the salt quite free from the alkali metals. It

* T. H. Laby, 'Phil. Mag.,' 1908, VI, vol. 16, p. 789.

† J. J. Thomson, 'Camb. Phil. Soc. Proc.,' 1907, vol. 14, p. 105.

was found that with this pure phosphate the positive emission, even at 1050° C., was very small, and Richardson therefore attributes the large emission from the commercial phosphate to the presence of alkaline impurities. Sir J. J. Thomson found that of all the classes of salts he experimented with the phosphates gave by far the largest emission of positive ions, which suggests that the emission is increased by the presence of phosphorus in the salt, and does not depend mainly upon the metal which happens to be combined with it. The importance of this point is so great that I decided to test some aluminium phosphate prepared in the same way as that used by Richardson. I am indebted to Mr. F. R. Ennos, B.A., and to Mr. W. W. P. Pittom, B.A., who prepared the salt for me in the Chemical Laboratory of this University. The precipitated phosphate, after washing with boiling distilled water, was divided into two parts, one of which was kept in a moist condition and the other was dried in an air oven. The former of these was the first sample of aluminium phosphate tested in these experiments, the dried portion was Sample No. III. It was found that each of these samples of pure aluminium phosphate gave an initial positive emission, which was considerably smaller than that given by either of the impure specimens. This confirms the observations of Richardson. It was also found, however, that after long-continued heating there was not much difference between the emissions from the different specimens.

In preparing the first aluminium phosphate anode tested, the platinum strip was covered on both sides with some of the pure sample which had been preserved in a moist condition. The strip was then gently heated in the air by means of an electric current, and the phosphate was thus dried and formed a thin uniform layer over the surface of the platinum. Anodes of the other samples were prepared in a similar manner; the platinum strip was first cleaned by careful scraping and washing, it was then covered with an emulsion made by mixing some of the new specimen with distilled water, and dried by gentle heating. In all cases when a new anode was fitted into the discharge tube, the air-pressure was reduced to a few millimetres, and the apparatus was left overnight in order that any moisture present might be absorbed by the drying tube.

With each of the aluminium phosphate anodes the first observations which were made were those of the rate of decay of the thermionic emission with time. The temperature of the anode was usually 1080° C., the potential difference was either 40 or 200 volts, the gas pressure in the apparatus was about 16 mm. With Samples I, III, and IV the current decreased continuously from the commencement of the experiment, but with

Sample II—the impure aluminium phosphate used by Sir J. J. Thomson in his experiments—the current steadily increased during the first half hour. It then gradually decreased for over an hour, when some sudden disturbance seemed to take place and in the next 20 minutes the current rose rapidly to its highest value, after which it decreased continuously to a fairly steady value in about three and a half hours. The rise in the current on first heating and the subsequent decay to a steady value is in agreement with the results obtained by Garrett, but this effect was not obtained with the other impure specimen tested in these experiments (Sample IV). This point will be referred to again later in the paper. In all cases after the first few hours' heating there was a gradual diminution in the emission throughout the experiments, but on leaving the apparatus overnight the current on the following morning was usually larger than when last tested. If the air pressure were several millimetres, the current at first would be about two or three times the normal value, and it would decrease to a steady value in about an hour. If an air pressure of only a small fraction of a millimetre had been left in the apparatus overnight, the effect already referred to with platinum was obtained, and the initial current on the following morning was perhaps 100 times the normal value. This large current always decreased very rapidly during the first few seconds of heating, afterwards falling off gradually to a steady value as in the case when the pressure was higher. It must be understood that the "steady" values were never quite constant; the current was always slowly decreasing as time went on, but when a "steady" value had been reached there was no appreciable alteration in the galvanometer deflection in the course of 5 or 10 minutes.

With both of the specimens of impure aluminium phosphate a curious effect was observed on first testing the emission after the anode had been left for some time in air at a pressure of several millimetres. Under these circumstances it was found that the initial current gradually increased for a few minutes before the usual decay to a steady value began. This effect was only noticed on one or two occasions when the pure salt was being tested; but, as will be seen later, it was also found to occur when a sodium phosphate anode was being used. When, after reheating an anode, a steady state of the emission had been obtained, the thermionic current was always slightly less than the steady value when last tested. It was therefore decided to test whether the current would decrease to a further extent if the anode were allowed to remain cold for several days. This was tested with Samples III and IV, and it was found that a very considerable diminution in the steady emission was produced by leaving the anode cold for two or three weeks with the air in the apparatus at a few millimetres pressure. It thus

appears that the change which causes the decay of the positive leak with time goes on even in the cold, though at a very much slower rate than when the anode is hot. It seems probable that this change is the evolution of gas by the anode, which one would expect to take place most rapidly at high temperatures.

With all four samples of aluminium phosphate the variation of the thermionic current with the potential difference was studied at different temperatures and with different gas pressures in the apparatus. The curves given in fig. 4 will serve to illustrate the results obtained. The

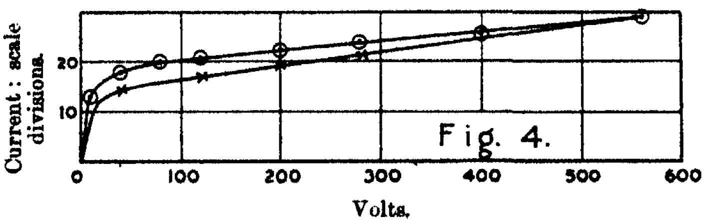


Fig. 4.

points marked ⊙ were obtained when the voltage was being gradually increased, those marked × were obtained afterwards, on decreasing the voltage. It will be seen that the currents under an increasing voltage were rather larger than those obtained under the corresponding decreasing voltage. There are two causes which tend to produce this effect. The first of these is the slow but gradual diminution of the emission with time, but that this does not account for the whole of the effect was proved by commencing the series with the highest E.M.F., gradually reducing it to zero, and then gradually raising it again to the initial value. Taking the observations in this order, the values of the current at increasing voltages were still much larger than the corresponding values with decreasing voltages, although the decay of the leak with time tends to equalise the values in this case. The second cause, and the one which seems to be mainly responsible for the hysteresis, is the fact that a sudden increase in the applied potential difference gives rise to a current which is at first larger than the normal value for that voltage, and which gradually decreases to the normal value in the course of 5 or 10 minutes. If the voltage is suddenly decreased the opposite effect takes place, the current to begin with is too small and gradually increases. A hysteresis effect similar to this was obtained by Richardson in his experiments with platinum.* In making the observations for a current-E.M.F. curve the readings have to be taken without much delay, firstly on account of the time-lag effect, secondly, because of the difficulty of maintaining the

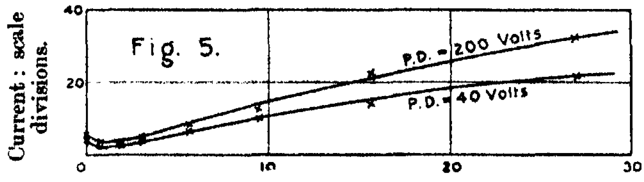
* O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 10.

temperature constant for a long time. At each change of the applied potential difference the new voltage was left on for about 2 minutes before the corresponding reading of the current was taken. The indications of the galvanometer showed that in this time a great part of the effect due to the sudden change of voltage had subsided, but it is probable that the current had not quite settled down to the steady value, and this causes each of the readings at increasing voltages to be slightly too high, and those at decreasing voltages to be slightly too low, thus accounting for the difference in the curves obtained under the two conditions. The curves in fig. 4 were obtained after the anode (Sample I) had been heated for several days at 1190° C., and the emission had become very small. The air pressure in the apparatus was 0·035 mm.; at higher pressures the curves rose more gradually, showing that a greater E.M.F. was required to produce approximate saturation of the current.

The relation between the thermionic current from aluminium phosphate and the air pressure in the apparatus has been investigated by Garrett,* who found that as the pressure was lowered from about 150 mm. the positive emission increased to a maximum value at somewhere between 15 mm. and 5 mm., according to the temperature of the phosphate, the maximum being at a lower pressure the higher the temperature. After passing through the maximum value the current rapidly decreased with the pressure and became very small in a good vacuum. In the present experiments a result similar to this was obtained with both specimens of impure aluminium phosphate, but with the pure salt the curves obtained were very similar to those given by platinum, and between 100 mm. pressure and a good vacuum there was no sign of the current attaining a maximum value. With all the samples experiments were made at 1080° C. and at 1190° C. At each temperature a series of readings was taken as soon as the positive leak became fairly steady, and other series were taken after the anode had been heated for many hours so that the emission at the particular temperature had been reduced to a low value. With Samples I and III of pure phosphate it was found that the current decreased gradually as the air pressure was reduced from its highest value; there was, however, little change in the emission at pressures above about 30 mm. At pressures lower than this there was a steady fall in the current to a minimum value between 1 mm. and 2 mm. pressure, followed by a slight increase as the pressure was still further reduced. When the observations were made at gradually increasing pressures precisely similar current-pressure curves were obtained. That the applied potential difference makes no appreciable difference to the general form of the current-

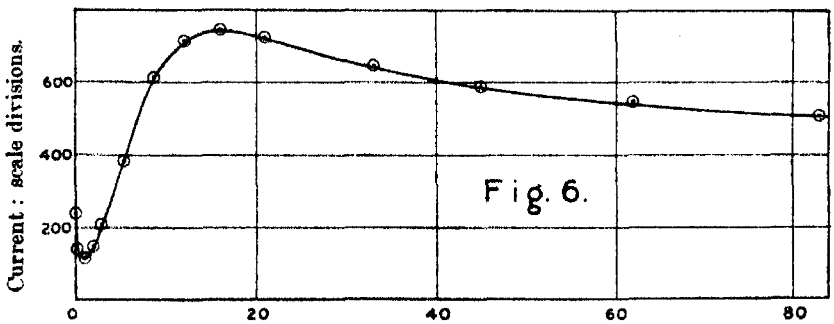
* A. E. Garrett, 'Phil. Mag.,' 1910, VI, vol. 20, p. 573.

pressure curves will be seen from the observations recorded in fig. 5. Here the temperature of the anode was maintained at 1190° C. and the air pressure in the apparatus was gradually decreased from 30 mm. to a low value. At each pressure observations were taken first with 40 volts and then



with 200 volts applied potential difference. It will be seen that under both conditions the current gradually decreased to a minimum value at about 1 mm. pressure, after which it increased slightly as the pressure was still further reduced.

When Samples II and IV of impure aluminium phosphate were used as anodes the current pressure curves resembled those obtained by Garrett, but at low pressures the current increased with diminishing pressure. This is well shown in fig. 6, which was plotted from observations at decreasing pressures made with the anode (Sample II) at 1190° C., and with an applied



potential difference of 200 volts. On pumping down from a pressure of 83 mm. the current slowly increased to a maximum value at about 19 mm. pressure, after which it decreased rapidly with diminishing pressure, attaining a minimum value at a pressure of about 1 mm., and then increasing somewhat on further pumping.

It was found that after an impure aluminium phosphate anode had been heated for a long time, the prominence of the maximum in the current-pressure curve became much less marked, and in the final set of readings, when the current had become very small, it increased continuously as the

air pressure in the apparatus was increased from about 1 mm. to 100 mm. At pressures below 1 mm. the curves were always similar to the corresponding portion of the curve in fig. 6. It seems, therefore, that the cause of the maximum current at a certain pressure gradually disappears on long-continued heating, whereas the cause of the increased leak at very low pressures still remains. This latter effect is the same as that recorded in the case of a platinum anode, an explanation of which has already been suggested.

A pressure of maximum thermionic emission had been obtained in these experiments only in the earlier stages of heating the impure aluminium phosphate; it was not observed in the experiments with the platinum anode, nor with the pure phosphate. It had, however, appeared to a very marked extent in some earlier experiments which had been made by the author with sodium phosphate, and thus it seemed possible that the maximum emission at a certain pressure was connected with the presence of sodium in the anode. In this case the gradual disappearance of the maximum on continued heating of the impure phosphate, ought to be accompanied by a disappearance of the sodium which is known to be present as an impurity in the fresh sample. In order to test this, at the conclusion of the series of current-pressure observations with Sample IV of impure aluminium phosphate, the apparatus was taken down, and the platinum strip, which was still covered with a white powder, was introduced into a non-luminous Bunsen flame. The flame did not give any evidence of the presence of sodium, but when a few grains of the original dry powder were placed on the strip, a yellow sodium flame was at once obtained. It thus appears that in the course of the experiments the sodium leaves the impure phosphate, an effect which may be due simply to volatilisation, or it may be an essential part of the mechanism of the large positive emission from the freshly heated anode.

After this flame test the anode was refitted into the apparatus, which was evacuated to a pressure of about 6 mm., and the thermionic current at 1190° C. was again tested by applying a potential difference of 200 volts. The initial current was $1{\cdot}26 \times 10^{-6}$ ampère; this decreased in the manner which is characteristic of the positive leak from freshly heated substances, and after about 90 minutes' heating was only $6{\cdot}3 \times 10^{-8}$ ampère, a value which was still somewhat greater than the last reading at this pressure before the flame test was made, namely, $2{\cdot}2 \times 10^{-8}$ ampère. The largely increased emission on first heating might possibly have been due to some of the powdered phosphate which had been heated in the Bunsen flame on the strip of platinum adhering to it and thus introducing a fresh supply of sodium. I did not consider this likely to be the cause, on account of the

small amount of fresh phosphate which was placed on the strip, but it seemed worth while to test the effect of heating in the Bunsen flame without risking contamination with sodium. Accordingly, on the following day, the anode was again heated to 1190° C., and was maintained at that temperature for nearly five hours, during which time the thermionic current decreased to $2 \cdot 5 \times 10^{-8}$ ampère. The apparatus was then taken down and the platinum strip was quickly and carefully introduced into a non-luminous Bunsen flame. Again there was no sign of the presence of sodium. After a few minutes' heating in the flame the anode was placed in position in the apparatus, and after pumping down the emission was tested under the same conditions as before. The initial current was greater than in the last experiment, being of the order of 10^{-5} ampère, but it decreased more rapidly, and in half an hour was no larger than it had been after 90 minutes' heating on the former occasion. On leaving the anode overnight, the emission was found to be less on the following morning, showing that, as usual, the change had gone on in the cold, and after heating for about an hour longer the current was reduced to a nearly steady value, $2 \cdot 9 \times 10^{-8}$ ampère, which is about the same as that obtained before repeating the flame test. We thus see that simply heating the platinum strip in the Bunsen flame had the effect of increasing the positive emission to a value which is about that of the freshly heated anode. It is well known that when platinum is heated in a flame it absorbs some of the flame gases, notably hydrogen, and there can be no doubt that it is the emission of these gases on subsequently heating in a vacuum which is responsible for the large current observed. This view is, at all events, in agreement with the rapid decay of this induced activity on continued heating, and with the fact that the decay is more rapid on repeating the experiment, for it would be expected that continually filling and emptying the platinum would have the effect of rendering the escape of the occluded gas more easy. That the sodium disappears from the anode during the experiments is extremely interesting, although it has been shown that the presence of this metal is not necessary in order to obtain a large positive emission, for there seems undoubtedly to be a connection between the presence of sodium in the anode and the variation of the thermionic current with the gas pressure in the apparatus. At all events, as far as these experiments go, on reducing the pressure of the air from about 60 mm., the thermionic current always increased to a maximum value at a certain pressure, depending on the temperature of the anode, when the latter contained sodium, and it did not do so in the absence of this metal.

The Experiments with Sodium Phosphate.

Experiments were made with two samples of Kahlbaum's sodium phosphate, and with one sample of Kahlbaum's sodium pyrophosphate. A long series of observations was only made in the case of one of the samples of sodium phosphate, for the tests made with the other salts showed that there was practically no difference in the thermionic emissions from the three samples. The results of a series of experiments with sodium phosphate at a temperature of 800° C. have already been published.* For purposes of comparison with the results for aluminium phosphate it was necessary to repeat the observations with sodium phosphate in air, at the higher temperatures 1080° C. and 1190° C.

The platinum strip after being carefully cleaned was covered with sodium phosphate by evaporating a water solution of the salt upon it. It was heated electrically during this process and the temperature was taken to a bright red heat to make sure that the salt was firmly attached to the platinum before the anode was placed in position in the apparatus. The thermionic current at 1080° C. under a potential difference of 200 volts was tested at a pressure of 55 mm. after an interval of 24 hours for the absorption of moisture by the phosphorus pentoxide drying tube. The initial current was $1 \cdot 7 \times 10^{-7}$ ampère, and this gradually increased during the first 40 minutes to $8 \cdot 4 \times 10^{-6}$ ampère, after which it decreased in the usual manner. The alteration of the initial current with time is thus similar to that which was found with one sample of the impure aluminium phosphate; it will be referred to again in the next part of this paper. Throughout the experiments it was found that after leaving the anode cold for some time with a considerable air pressure in the apparatus the effect which has been mentioned in connection with impure aluminium phosphate occurred, the current on retesting increased for the first few minutes and then the decay continued. The maximum current was usually smaller than the last reading of the previous evening, showing that the change which causes the decay of the emission had gone on in the cold. The proportional amount by which the activity of the anode was reduced by allowing it to remain cold was somewhat variable, but it seemed to depend in the main upon two things, firstly, upon the total length of time during which the heating had been kept up, and, secondly, upon the interval since the last observation was made. The experimental results were in agreement with the assumptions that the freshly heated anode evolves a gas which takes part in carrying the current, and that the gas is also evolved, though at a very much slower rate, when a new anode is allowed to remain cold in a good vacuum.

* 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 89.

On those occasions when the apparatus was left unused for some time with the gas pressure very low, the initial current was usually very large but decreased in a few seconds to a much smaller value, which gradually increased and then decreased in the manner described above. This large leak at the start is the effect which was nearly always obtained on leaving any anode cold for some time in a good vacuum, and which I have suggested is due to the action of mercury vapour upon the platinum strip.

The relation between the current and the applied potential difference was investigated with different gas pressures in the apparatus, at both 1080° C. and 1190° C. The general character of the results obtained was precisely similar to that of the results recorded in the account of the experiments with aluminium phosphate. Measurements of the positive emission under a constant potential difference of 200 volts were made with both increasing and diminishing pressures of air up to about 60 mm. The first series of observations was made at 1080° C. after about 10 hours' heating at that temperature, and a maximum value of the thermionic current occurred at a pressure of 12 mm. when the pressure was being gradually reduced, and at about 15 mm. with increasing pressures. Similar results were obtained at the higher temperature, 1190° C., but here the pressure of maximum emission was not so well marked, probably because the anode had been heated for a long time before observations at this temperature were made. A similar effect was noticed in the experiments with aluminium phosphate containing sodium, but in that case the pressure of maximum emission could not be detected after long-continued heating, whereas in the present case the thermionic current always had a maximum value at a pressure of about 10 mm. when the temperature of the anode was 1190° C. That the variation of the current with the gas pressure became much reduced by continued heating at 800° C. was pointed out in the account of my earlier experiments with sodium phosphate. In the case of impure aluminium phosphate, the removal of the pressure of maximum emission by continued heating was accompanied by the disappearance of sodium from the anode. In the present experiments, although the amount of sodium phosphate on the anode was less at the conclusion of the experiments than it had been at the beginning, it did not completely disappear—a fact which was also obvious from the magnitude of the positive emission.

The thermionic current from impure aluminium phosphate is at first larger than that from sodium phosphate under similar conditions, but on continuing the heating for some time, the current from aluminium phosphate falls off to a much lower value than that from sodium phosphate. At the end of the experiments with the latter salt the current at 1190° C. in an air pressure of 10 mm. was about 450 times the final value from impure aluminium

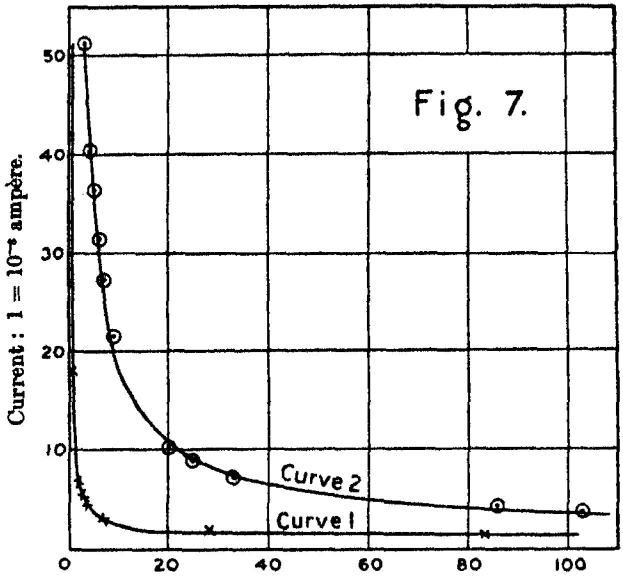
phosphate. The existence of this large emission from an anode which has been heated for so long that most of the occluded gas must have been driven out of it, is evidence in favour of the view that at this stage the current is largely carried by sodium atoms.

At low pressures the thermionic current from sodium phosphate always decreased continuously as the pressure was reduced. There was never any sign of the increasing current obtained in other cases. This is accounted for by the greater emission in the case of this anode, which would completely mask an increase of the magnitude usually observed.

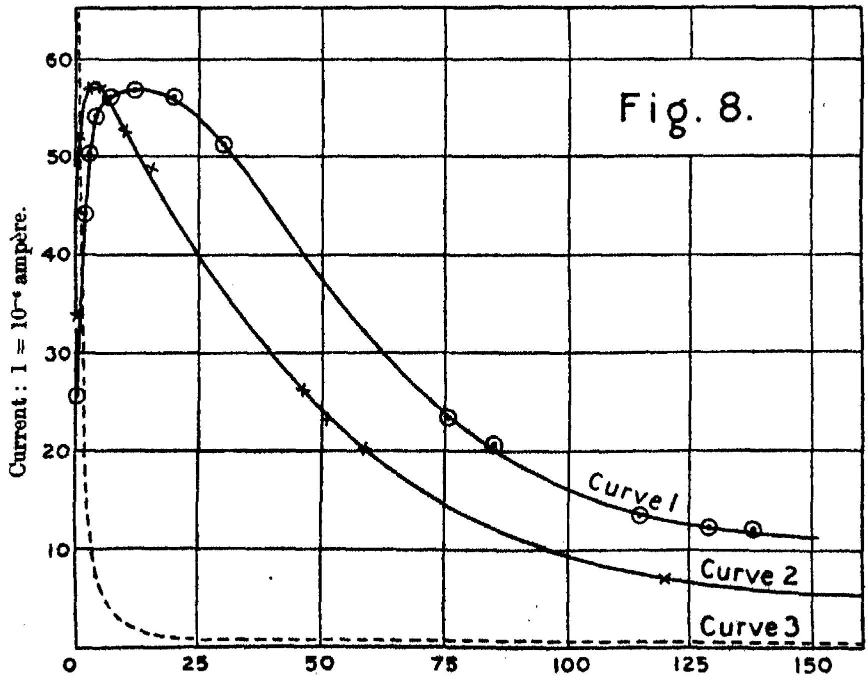
The Decay of the Positive Emission from Freshly Heated Anodes.

The thermionic emissions from the various anodes, when freshly heated, cannot in all cases be compared, because the conditions under which the initial tests were made were not always the same. In the case of platinum itself, and of the first samples of aluminium phosphate, observations were made at the lowest temperature at which a conveniently measurable current was obtained, whereas with the later salts the observations were commenced at 1080° C. With a view to comparing the initial currents from the different anodes, and the rates of decay under similar conditions, a fresh series of observations was made at the highest temperatures used in these experiments, 1190° C., the air pressure being in all cases 15 mm., and the potential difference 200 volts. The platinum strip was well washed to free it from sodium phosphate. It was then dried, and the absence of sodium was proved by heating it in a Bunsen flame. The anode was replaced in the apparatus and the decay of the initial current from platinum under the standard conditions was investigated. The values of the currents during the first two hours are plotted in Curve I, fig. 7, and in the same diagram the corresponding curve for pure aluminium phosphate is given (Curve II). In this latter case, the current during the first few minutes was too large to be included in the figure, but the emission decreased continuously from the start, very rapidly at first, and the curve when plotted to a smaller scale was exactly similar to the curve for platinum.

The decay curves for the emission from sodium phosphate, from sodium pyro-phosphate, and from impure aluminium phosphate are given in fig. 8, the curves being numbered in that order. The Curves I and II for the sodium salts show the characteristics which have already been described, namely, an emission which increases to a maximum value during the first few minutes and then decays away. The curve for impure aluminium phosphate (Curve III) is similar to those given in fig. 7 for the pure phosphate and for platinum; there is an enormous decrease in the current



Time from beginning of heating (minutes).



Time from beginning of heating (minutes).

during the first few minutes. The salt with which this curve was obtained was from the same bottle as Sample IV in the experiments already described, and the decay curve is similar to that which was obtained before with the anode at 1080° C. It will be remembered that the other specimen of impure aluminium phosphate (Sample II) gave a result resembling that obtained with the phosphates of sodium, the decay being preceded by an increase in the current to a maximum value. This initial increase in the current before the decay sets in was not only obtained with these anodes when new, but also, to a smaller extent, on reheating after they had been left cold for some hours in a pressure of several millimetres of air. A preliminary increase of the emission on reheating under these conditions was also occasionally noticed when the anode consisted of pure aluminium phosphate, or of platinum, although the magnitude of the effect in these cases was very small. The aluminium phosphate used by Garrett in his experiments* also gave an initial current which increased to a maximum in about eight minutes, and then decreased rapidly. He points out that the form of the curve seems to indicate that the first effect of the high temperature is the production on the anode of an unstable substance, which does not itself emit ions, but which gives rise to a second unstable substance which is the origin of the ionisation.

In the following table I have collected together the values of the thermionic currents from the different anodes at the commencement of the heating, and after the temperature (1190° C.) had been maintained for 1, 2, 10, 50, and 100 minutes:—

Anode.	Current in 10^{-8} ampères.					
	At start.	1 min.	2 mins.	10 mins.	50 mins.	100 mins.
Platinum	183	18·0	6·9	2·5	1·74	1·24
Pure aluminium phosphate	2040	201	87	18·0	5·6	3·6
Sodium phosphate	2550	3350	4430	5650	3750	1600
Sodium pyro-phosphate	3380	5220	5600	5270	2400	940
Impure aluminium phosphate	7560	3220	1450	250	59	32

The values of the current at the start must be taken as being approximate only, for the rapidity of the alteration during the first minute makes the observation very difficult. The numbers given for platinum and for the phosphates of aluminium were obtained from the largest deflection of the galvanometer, and the rapidity with which this indicates changes in the

* A. E. Garrett, 'Phil. Mag.,' 1910, VI, vol. 20, p. 573.

current depends on the extent to which it is shunted. The instrument was shunted to the same extent for the measurements with platinum and with pure aluminium phosphate; a shunt of smaller resistance was used in the cases of impure aluminium phosphate and of the phosphates of sodium.

From the numbers in the above table it will be seen that the decay of the current during the first minute of heating is much the greatest with a platinum or a pure aluminium phosphate anode; with the aluminium phosphate containing sodium the decrease is considerably smaller, and in the case of the phosphates of sodium the current increases. Now it is remarkable that when an impure aluminium phosphate anode which had been used for so long that all traces of sodium had disappeared from it was heated for a few minutes in a Bunsen flame, the emission on retesting was found to be of the same magnitude, and to decay during the first few minutes in the same rapid manner, as the initial discharge from the freshly heated pure salt. The increase of the current after heating in the Bunsen flame is, no doubt, due to the emission of gases which have been absorbed from the flame, and this points to the conclusion that the large initial currents from freshly heated platinum and from pure aluminium phosphate are also due to the emission of gases by these anodes. There is doubtless an emission of gas also in the case of the other anodes used, and this is probably responsible for carrying some of the observed current, but in these cases there is apparently some other source of ionisation which increases either in amount or in activity, or in both respects, during the first few minutes' heating, and the most probable origin of this effect seems to be the sodium which these anodes contain. In the case of impure aluminium phosphate this second source is not very large, and serves only to decrease the rate of decay of the total emission; with the phosphates of sodium, however, the decay is completely overcome, and there is an increasing current during the first few minutes. It will be remembered that an initial increase in the current was also observed with Sample II of impure aluminium phosphate. This would seem to indicate that Sample II contained a greater amount of sodium impurity than Sample IV, which was used in obtaining the figures in the above table. After a very few minutes' heating the decay of the emission from the impure salt is more rapid than the decay of the activity of the pure phosphate, a state of affairs which can readily be explained by the gradual disappearance of the sodium, in addition to the falling off of the gas emission, in the case of the former anode.

The numbers recorded in the table give the relative activities of the different substances at 1190° C. The observations which had been made at lower temperatures gave the same general result. The largest initial current

was always given by impure aluminium phosphate, and next in order of thermionic emission come the phosphates of sodium, pure aluminium phosphate, and, last of all, platinum. The initial increase in the emission from sodium phosphate was relatively larger, and continued for a longer time, when the anode was at 1080° C. than when it was heated to 1190° C., a result which is probably due to the rate of evolution of gas from the heated anode increasing very rapidly with rise of temperature.

A comparison of the final values of the thermionic currents from the different anodes after heating for a long time is given in the following table. In all cases the applied potential difference was 200 volts, and the temperature 1190° C.:—

Anode.	Thermionic currents ($1 = 10^{-9}$ ampère) at various air pressures.					
	0·005 mm.	1 mm.	2 mm.	5 mm.	10 mm.	20 mm.
Platinum	5·2	1·65	1·65	2·2	2·9	3·9
Pure aluminium phosphate	0·7	0·6	0·7	0·9	1·2	2·0
Impure aluminium phosphate	2·9	1·5	2·0	3·1	4·1	5·0
Sodium phosphate	1080	1500	1630	1750	1810	1740

The numbers given are interesting as indicating the order of magnitude of the emission from the different anodes at the conclusion of the experiments, but too much importance should not be attached to the actual figures, for it must be remembered that there was every indication that continued heating would have reduced the emission still further, although the rate of decay of the current had become so small that, in the case of the salt anodes, it might perhaps be accounted for by the phosphate gradually becoming detached from the platinum. From the table it would appear to be doubtful whether the small emission given by pure aluminium phosphate is due to that salt at all, for it will be seen to be smaller than the emission from the platinum strip itself at the beginning of the experiments, but this would have decreased considerably during the extra heating. At the conclusion of the experiments with the phosphates the platinum strip was cleaned and tested alone; it was found that after heating at 1190° C. for several hours, the thermionic currrent was reduced to a smaller value than any recorded in the above table, and I am therefore inclined to think that the numbers given for pure aluminium phosphate are in part due to some remaining small emission from that salt. After heating for about the same length of time, the final current measured from the impure aluminium phosphate is not much greater

than that from the pure salt, although during the course of the first few minutes' heating it was more than fifteen times as great. It has already been stated that this seems to be due to the disappearance of the sodium which was present as an impurity in the former anode. The outstanding feature of the above table is the relatively enormous emission from sodium phosphate, which is obtained although the anode had been heated for at least as long as either of the specimens of aluminium phosphate.

The Nature of the Carriers of the Positive Thermionic Current.

The experiments described in this paper have shown that there are considerable variations, both in the magnitude, and in the permanence, of the positive emission from different substances. In the case of platinum, and of pure aluminium phosphate, we have an initial thermionic emission which decreases very rapidly with time, and in the course of a few hours' heating at a high temperature becomes extremely small. With sodium phosphate, on the other hand, the emission at first increases, and then decreases much more slowly than with the other substances tested, so that even after many hours' heating a very considerable thermionic current can be obtained. The impure aluminium phosphate falls between these two cases. At the commencement of the heating the alteration in the emission with time resembles that given by phosphate of sodium, whereas the final low value more nearly corresponds to the current from the pure phosphate or from platinum. The experiments have shown that this is accounted for by the fact that in the beginning the impure phosphate contains sodium, but that this gradually disappears from the anode in the course of the heating. The author is of opinion that the ionisation from platinum (and from metals generally) is largely due to the emission of absorbed gases on heating, but that in the case of sodium phosphate a considerable part of the emission consists of positively charged sodium atoms, the final value of the current in a good vacuum after long-continued heating being almost entirely due to this cause, although at first there is no doubt also a large current due to the evolution of ionised gas, which probably comes partly from the salt and partly from the platinum upon which it is heated.

That certain salts of sodium when heated and used as anodes in vacuum tubes emit positively charged sodium atoms was demonstrated by Gehrcke and Reichenheim in the year 1906,* but the experimental conditions were somewhat different from those described in this paper. In their earlier experiments the salts were heated upon platinum foil, but the cathode of the discharge tube was also heated electrically, and consisted of a platinum

* Gehrcke and Reichenheim, 'Deutsch. Phys. Ges. Verh.,' 1906, p. 559.

strip covered with barium oxide. The potential difference applied was 110 volts, and under these circumstances a bundle of yellow rays was seen proceeding from the salt on the heated anode. These rays Gehrcke and Reichenheim called "anode rays," and subsequent experiments proved them to consist of positively charged sodium atoms. In later experiments* Gehrcke and Reichenheim obtained better results by using much higher potential differences across the tube and having neither electrode heated by an external current; the current sent through the tube by the applied E.M.F. gradually warmed up the salt anode, and when this attained a bright red heat a luminous pencil of rays could be seen proceeding from it. The discoverers of these rays found that they were given particularly well by the haloid salts of the alkali metals. In each case the value of the specific charge of the ions, which was measured by two different methods, agreed with the value calculated on the supposition that they consist of atoms of the metallic constituent of the salt under test, conveying a charge equal to that carried by the hydrogen ion in electrolysis. Anode rays were also obtained from salts of the divalent elements strontium and calcium, and in these cases the carriers appeared to be doubly charged atoms of the metal used (Sr_{++} or Ca_{++}). For a full account of the methods of obtaining these anode rays reference must be made to the original papers, but it will be convenient to mention here some of the conditions which seemed to favour their production. In the earlier experiments, in which the salt was heated upon platinum foil and a low potential difference was used, the rays lasted for a very few minutes only. In the later form of apparatus, in which a small stick of the fused salt formed the anode, the rays could be obtained for several hours, although the activity diminished with time. The length of the luminous ray was greater the higher the vacuum in the discharge tube, but where the path was non-luminous it could be traced by the fluorescence produced on the glass. The most copious supply of rays was obtained when easily dissociating or volatile salts were used as anodes, and some mixtures of salts seemed to work better than either of the constituents alone, possibly because the mixture had a lower melting point. Anode rays could not be obtained from a cold anode, and in the form of apparatus where no external heating was used it was necessary to wait some time after the high E.M.F. was applied, until the current through the tube had raised the extremity of the anode to a red heat, before the rays appeared.

It occurred to the author that the anode rays of Gehrcke and Reichenheim were essentially the same as the thermionic emission from heated salts. Sir J. J. Thomson had found that the greatest emission was given by phos-

* Gehrcke and Reichenheim, 'Ann. der Phys.,' 1908, p. 861.

phates, and that aluminium phosphate was particularly active. It was therefore attempted to obtain anode rays from this substance, but without success.* A mixture of phosphates of sodium and lithium was also tried, and in this case some curious luminous effects were obtained, but I was unable to see the fine bright pencils of light described by their discoverers as characteristic of anode rays. It was, however, obvious that positively charged sodium was being shot off from the anode, for, although the cathode was behind the anode, so that anything shot out by the glowing phosphates was projected away from it, yet a bright yellow sodium light began to appear on the cathode as the tube was worked, appearing first on the edge nearest to the anode, and gradually spreading all over it. The impossibility of obtaining anode rays from these salts, which were then thought to be the most copious emitters of positive electricity when heated, led the author to the conclusion that there was no close connection between the two phenomena. Recent researches, however, have modified this opinion. Richardson has determined the specific charge of the carriers of the thermionic current from a number of different salts when heated *in vacuo*, and has concluded that these carriers are atoms of the respective metallic constituents minus a single electron. He also found that aluminium phosphate is by no means the most active salt in producing positive ionisation when heated in a vacuum, a result which is confirmed by the experiments recorded in the present paper. In the light of these results it seems probable that the anode rays of Gehrcke and Reichenheim are essentially the same as the emission, in a good vacuum, from a positively charged salt which has been heated until the steady state is reached. There is, however, the difference that in the anode rays the emitted atoms are travelling much faster owing to the fact that they are liberated into a much stronger electric field. Gehrcke and Reichenheim have shown that it is necessary to have a large fall of potential at the anode in order to obtain luminous anode rays. Under ordinary circumstances, with such gases as oxygen or nitrogen in the discharge tube, the anode fall of potential is about 20 volts, and the velocity which the ions attain is too small for luminosity to result, but if a small quantity of any halogen vapour is introduced into the tube, the anode fall increases enormously, and may become many thousands of volts. This fact explains why anode rays are readily obtained when haloid salts are used which have the property of dissociating when strongly heated. Now Richardson has concluded from his experiments† that what is required for a salt to be a good emitter of positive ions "is a

* 'Camb. Phil. Soc. Proc.,' 1909, vol. 25, p. 329.

† O. W. Richardson, 'Phil. Mag.,' 1911, VI, vol. 22, p. 669.

combination of volatility in the possible compounds formed, together with high electro-positiveness of the metallic constituent." The salts of the alkali metals he found to be particularly active, and if only a trace of either sodium or potassium were present as an impurity in the salt under test, the values of e/m obtained for the positive ions always indicated that they consisted of atoms of these metals. Volatile salts were found to be more efficient than non-volatile salts; for instance, zinc haloids were very active, and barium sulphide was more efficient than barium sulphate. It will thus be seen that the class of salt which is best from the point of view of thermionic emission with low potential differences is precisely that which was found by Gehrcke and Reichenheim to be most efficient for the production of anode rays. The carriers of electricity in the two cases are identical, the only difference seems to be in the velocity with which they travel. It should, however, be mentioned that whereas Gehrcke and Reichenheim found that the anode rays from salts of strontium and calcium consisted of atoms of these metals carrying double charges, Davisson* obtained a value for the specific charge of the carriers of the thermionic current from these salts corresponding to a single unit of electronic charge per atom. In some more recent determinations of e/m for strontium anode rays by measurements of the Döppler effect, Reichenheim† obtained from certain lines of the spectrum a value corresponding to Sr_{+}, and from other lines a value more nearly corresponding to Sr_{++}. Also Richardson has concluded that there are ions of the type Zn_{++} present in the thermionic emission from the zinc haloids. There is evidence, therefore, both in the case of anode rays, and of the ordinary thermionic emission, that polyvalent atoms may carry either single or multiple charges, but further investigation of this point is required before it can be regarded as fully established.

My experiments on the discharge of positive electricity from sodium phosphate heated in different gases led me to the view that the gas present in the discharge tube takes an active part in carrying the thermionic current—probably by diffusing into the anode and being emitted in an ionised condition. This view has been criticised by Richardson,‡ who holds that the carriers of the thermionic current are in all cases atoms of the metallic constituent of the salt under test; a conclusion which he bases upon his determinations of the value of the specific charge of the carriers in a good vacuum. I think there can be little doubt that when a salt anode has

* C. J. Davisson, 'Phil. Mag.,' 1912, VI, vol. 23, p. 121.

† O. Reichenheim, 'Ann. der Phys.,' vol. 33, p. 747.

‡ O. W. Richardson, 'Phil. Mag.,' VI, vol. 22, p. 669.

been heated for so long that the thermionic emission has decreased to what I have called its "steady value," the carriers of the current in a good vacuum are mostly metallic atoms—the ions which have been found by Gehrcke and Reichenheim to constitute the anode rays. At higher gas-pressures there is a considerable increase in the thermionic current, corresponding presumably to an increased emission of positively charged ions from the heated anode. On the view which is advocated by Richardson no part of the current is carried by the gas, and this increased emission consists solely of positively charged atoms of the metallic constituent of the salt, but, so far as the author is aware, no theory has been advanced which explains how the presence of the gas increases the emission of these atoms. The theory that the ions are entirely metallic atoms seems to rest upon some experiments of Davisson,* by which he claims to have proved (1) that the gases emitted by a heated anode are uncharged, (2) that the increased thermionic emission from a salt which is caused by the presence of a gas is not due to the cause which I suggested in the paper referred to above. The first of these conclusions is in direct opposition to the results of other observers. In the case of aluminium phosphate heated upon platinum, Garrett, from observations of e/m, concluded that some of the carriers were charged hydrogen atoms, and the earlier work of Richardson on the positive discharge from heated platinum led him then to the view that the gas emitted by the hot metal was ionised. Richardson investigated the positive leak from the outer surface of a platinum tube heated electrically in air at atmospheric pressure, while hydrogen was diffusing through the walls of the tube from the inside. The results showed that the effect of the hydrogen was "to produce an additional number of positive ions proportional to the amount of hydrogen diffusing out," from which Richardson concluded that "the hydrogen inside the metal, which is known from other considerations to be in the atomic state, is positively charged," although "only a small fraction of it comes out in the ionic form."† These experiments are strong evidence in favour of the view that the carriers of positive electricity from heated platinum which is evolving hydrogen consist, partly at all events, of charged atoms of that gas, and it would seem to be extremely probable that the carbon monoxide gas which is generally evolved by a heated anode is also emitted in an ionised condition. Of course, it does not follow that since the gases emitted by a metallic anode are ionised, that those emitted by salt anodes are also ionised, though I think this is usually the case, but it must be remembered that in the usual method of testing the thermionic emission, the salt is heated

* C. J. Davisson, 'Phil. Mag.,' VI, vol. 23, p. 139.

† O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 58.

upon a strip of platinum and there is doubtless a liberation of ionised gas from this. It was probably hydrogen evolved in this way from the platinum strip which was detected in the determinations of e/m for the ions in Garrett's experiments.

Davisson's second conclusion—that the increase in the thermionic current from a salt which is caused by the presence of gas, is not due to the emission of gas atoms or molecules which have been absorbed by the salt and are emitted in a charged condition—rests upon determinations of the specific charge of the carriers from impure aluminium phosphate, in air and in carbon monoxide at pressures of about 0·1 mm., and in hydrogen at about 1 mm. pressure. The temperature of the anode was 600° C.; the first observed value of e/m in a good vacuum was taken to indicate that the ions were charged potassium atoms. After longer heating the value found was much nearer the specific charge for sodium, and the ions were taken to be atoms of this metal. On allowing gas to enter the apparatus the difficulty of measuring the specific charge of the carriers increased, owing to the scattering which occurs on collisions with the gas molecules, and Davisson concludes that this effect is responsible for the much smaller values which are then obtained. From the curves given it appears that, with carbon dioxide, for example, the value of e/m decreases from about 435 in a good vacuum to 280 at a pressure of 0·13 mm. (The value of e/m for Na_+ is 421, and for CO_{2+} is 243.) If an alteration of this magnitude is produced by the interference of the gas with the free passage of the ions, it is obvious that the method employed is quite unsuitable for determining the value of the specific charge of the carriers at the higher pressures. Moreover, previous to these experiments of Davisson, Garrett had shown that in the case of an aluminium phosphate anode at 1005° C., an increase in the gas pressure of the order used by Davisson produces only a very slight increase in the thermionic emission, and the increase would be very small indeed at the much lower temperature used by Davisson. In the experiments recorded in this paper it was found that the emission actually decreases slightly as the gas pressure is gradually raised to about 1 mm., so that if accurate measurements of e/m could be made at this pressure they would not be expected to indicate that the gas is carrying any larger proportion of the current than it does at lower pressures.

Reference has been made at the commencement of this paper to the view recently advocated by Richardson as to the nature of the positive ions from incandescent metals. Richardson obtained values of the specific charge of the ions from different metals varying from 486 to 337, the mean value from measurements with 13 metals giving 25·7 for the mass of the carriers

as compared with the mass of the hydrogen atom, from which he concludes they are atoms of sodium or potassium.* My experiments with impure aluminium phosphate have shown that if when first heated an anode is contaminated with sodium impurities, these disappear after the thermionic emission has been going on for some time, so that it is improbable that the value of the specific charge measured under these conditions refers to sodium atoms. As the result of a determination of e/m for the carriers of positive electricity from a hot platinum wire, Sir J. J. Thomson some time ago came to the conclusion that the current is carried both by atoms of the metal and by atoms or molecules of the surrounding gas.† Richardson, in his experiments, did not detect any ions of the former type, but his value of e/m for the carriers is not inconsistent with their being molecules of carbon monoxide carrying single charges (CO_+). It is known that many metals evolve this gas when heated, and that it is continually being set free in an evacuated vessel which contains traces of wax or grease, so that its presence in the apparatus used by Richardson is easily accounted for.

I think there can be little doubt that the large emission on first heating a clean platinum anode is due to escaping gas which comes from inside the metal in an ionised condition. The connection between the gas emission from heated metallic wires and the emission of positive electricity from them has been carefully studied by Klemensiewicz.‡ He found that wires which had been heated in a good vacuum until the thermionic emission was very small, regained their activity when they were allowed to stand for some time in a gas at a pressure of several atmospheres, and that the recovery was aided by keeping the wires at a temperature of about 200° C. so as to assist the diffusion of the gas into the metal. On the other hand there was no recovery of activity when the wires were allowed to remain for a much longer time in an evacuated glass tube. There is thus a very close connection between the positive ionisation and the emission of absorbed gas, and this connection is most simply explained by the view that gas coming from the interior of the wire is ionised. It is difficult to see any explanation on the supposition that the ions are atoms of sodium or potassium. If the gas actually carries the current, we see at once the cause of the rapid fall of the emission from a new wire, for when the wire is heated the gas pressure inside it is increased and the gas diffuses out until there is equilibrium between the internal and the external conditions. When, after

* O. W. Richardson, 'Phil. Mag.,' 1910, VI, vol. 20, p. 545.

† J. J. Thomson, 'Conduction of Electricity through Gases,' Camb. Univ. Press, 1903, p. 185.

‡ Z. Klemensiewicz, 'Ann. der Phys.,' 1911, vol. 36, p. 796.

long-continued heating, equilibrium is attained, there are as many gas atoms or molecules entering the wire in a given time as there are emitted by the wire. The latter are ionised, a certain proportion of them (probably a very small proportion of them) is positively charged, and it is the charges carried by these which constitute the small "steady" current which is given by a wire which has been heated for a long time. This is the view of the emission of positive ions from heated metals which the author thinks is most in agreement with the experimental results; at the same time, if the metal is not perfectly clean, or if there are gases or vapours present which have chemical action upon it, there is probably a certain amount of ionisation produced in other ways. If there is a trace of sodium or of potassium impurity on the anode, then it is probable that atoms of these metals assist in carrying the current as they do when a salt anode is used. In the experiments with platinum described in this paper the metal was very carefully cleaned before being tested, and later in the research it was found that the usual large emission on first heating was obtained after the platinum had been heated in a Bunsen flame, although the flame gave no evidence of the presence of sodium. I think, therefore, that the ions cannot be sodium atoms in this case.

A small amount of chemical action may give rise to considerable ionisation, and so if gases or vapours are present which have a chemical action on the anode there may be electrification produced while this action is going on. It seems probable that some of the ionisation which is produced when certain salts are heated has its origin in chemical actions between vapours produced by these salts and the platinum on which they are heated. This view has already been put forward by Richardson to explain certain ionisation effects which he obtained when various salts were heated to a high temperature in a platinum tube.

The author wishes to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus used in these experiments, and also to Prof. Sir J. J. Thomson for his advice and kindly interest in the research, which was carried out in the Cavendish Laboratory.

Ionic Size in Relation to Molecular Physics, together with a New Law Relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules.

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CONTENTS.

1. *Introduction.*—The greater part of this communication is concerned with obtaining the volumes and densities of the ions and ionic nuclei of three salts (KCl, NaCl, LiCl) from conductivity, viscosity, and freezing-point data, a process which is of limited interest and is therefore reserved for the later sections of this communication. The deductions which are drawn from the values so obtained, in conjunction with other data already available, lead to certain conclusions as to the heats of formation both in the solid and ionic state which are of much wider interest and are dealt with in the next section.

In two former communications* there was developed a theory with reference to the ascertainment of the relative sizes of ions which was based upon a consideration of various physical data relating to KCl and NaCl. In the present paper the necessary data are given for extending the results to LiCl. In the former papers an empirical linear relationship was found between the solution volumes calculated from density measurements and the ionic volumes deduced from conductivity and viscosity measurements, which is now extended to LiCl. In the present paper a new empirical relation will be found between the ionic volumes and the reciprocals of the effective

* I shall have necessity to refer from time to time to these papers, and will do so under the short names "Ionic Sizes I" and "Ionic Sizes II." An abstract of the former is to be found in 'Roy. Soc. Proc.,' 1905, p. 563, but the references herein given are to the full paper, which was published, with some additions, in the 'Zeit. für Phys. Chem.,' 1905, vol. 53, p. 257. The second paper was published in 'Phil. Trans.,' 1906, A, vol. 206, p. 101. For the understanding of the later sections of the present communication it is necessary that the reader should have the second paper before him.

molecular freezing-point depressions* of the three salts in question. These two sets of empirical relations are found to be capable of simple theoretical interpretations, and to yield in combination interesting information as to the relative volumes and densities of the ions and of the ionic nuclei.

The three salts above mentioned are compounded of some of the most *compressible* of the *elements*, and are therefore admirably suited for a consideration of volume changes in relation to heats of formation.

Now that we are coming to regard an atom as being itself composed of hundreds of more minute bodies (which we will designate as corpuscles, in order to adopt a neutral term) there is no *a priori* improbability in the theory of the compressibility of atoms. We shall therefore express our results in terms of this hypothesis, to which they appear to give considerable support.

In order to correlate changes of atomic volume with heats of formation, it was necessary to consider a wider group of compounds of the same class as the three salts above mentioned. For this purpose certain available data exist within a sufficient area to enable a useful generalisation to be made. These data lead us to a new law relating to the heats of formation of the solid and liquid compounds formed from the elements and radicles of the substances considered, which may be enunciated as follows:—

The heat of formation due to the combination in the liquid or solid state of any of the electro-positive elements with any of the electro-negative elements or radicles is approximately equal to the sum of certain calorific constants of the two elements or radicles, together with $0{\cdot}875\ \delta V$, where δV is the change of atomic volume produced by the combination.

This leads us to the conception of the internal energy of an atom as the sum of the kinetic energy of the corpuscles and of their potential energy under their mutually attractive forces. On this view, the heat component, $0{\cdot}875\ \delta V$, represents the change in the internal energy of the atoms due to their volume changes on combination.

The heats of ionisation of KCl, NaCl, and LiCl are apparently irregular and have not hitherto been regarded as periodic functions of the atomic volumes. The application of the factor 0·875 to the contraction of volume of the nuclei will be found to show the heats of ionisation as periodic functions.

It further appears probable that we can bring the heat of ionisation into complete subordination to the same general law as that above enunciated for the solid and liquid compounds of the same class.

* In a former paper (Ionic Sizes II, p. 142) I used this expression to indicate the so-called molecular depression Δ/N divided by $(1+\alpha)$, where α is the ionisation coefficient. The effective molecular depression of the freezing point may be shortly indicated by the letters E.M.D., so that the E.M.D. is $\Delta/N\,(1+\alpha)$.

2. *Components of Heats of Formation of Solid, Liquid, and Ionic Molecules.*—Sufficiently complete data are available for most of the compounds of H, K, Na, and Li, with the radicles Cl, Br, I, NO_3, IO_3, to enable us to arrive at a generalisation within this limited area as to the relation between heats of formation and atomic volumes. The values of the atomic volumes of the elements in the uncombined state are indicated by the letter V, and are set out at the foot of the table. The values are those given by Mendeléeff, with the exception of those for K, Na, and Li, for which the values are those given by Richards based on his own density determinations.* The atomic volumes of the positive elements of each compound are set out in the column headed V_1, and those of the negative radicles in the column headed V_2. The values given for the compound radicles, such as NO_3, are merely the sums of the atomic volumes of their components. The column headed V_1+V_2 gives the sums of the atomic volumes of the elements in each compound. Under ρ are given the densities of the solid and liquid compounds, and under W their atomic weights. The quotient W/ρ is therefore the actual molecular volume of each compound. The difference V_1+V_2-W/ρ is the contraction of volume for each molecule which takes place on combination, and is set out in the column δV. The actual heats of formation in kilogramme-calories from Thomsen's data are given in the column headed H.F. It will now be seen from the table that each heat of formation is the sum of three quantities, viz., a part which is proportional to the total contraction, and is expressed by $0{\cdot}875\ \delta V$, and a remainder which is the sum of two components H_1 and H_2, which have approximately the same value for each radicle in every combination. To split the additive components into two parts H_1 and H_2 we require a definite starting-point, which is wanting. It is obvious, however, from the heats of formation of HCl, HNO_3, and HIO_3 that the calorific constant for the hydrogen atom is comparatively small. If we place it at 1 then the calorific constants for the other radicles are those given under "Values of H" at the foot of the table. If the value of H_1 for hydrogen were 3 instead of 1 we have only to diminish the heat components H_2 for each of the negative radicles by 2, and increase the heat components H_1 for the positive radicles by the same amount. It must, therefore, be understood that the value of 1 for the heat component for hydrogen is arbitrary, but it makes no difference to the additive scheme. The result is that all the heats of formation may be approximately expressed as

$$\Sigma = 0{\cdot}875\,\delta V + H_1 + H_2.$$

The separate components are set out in three columns of the table and the

* 'Journ. Amer. Chem. Soc.,' 1909, vol. 31, p. 156.

Table I.—Components of Heats of Formation of Solid and Liquid Compounds.

	V_1.	V_2.	V_1+V_2.	ρ.	W.	W/ρ.	δV.	$0{\cdot}875\,\delta V$.	H_1.	H_2.	Σ.	H.F.	Diff.
HCl	12·0	27	39·0	0·85	36·5	43·0	−4	−3·5	1·0	24·3	21·8	22·0	−0·2
KCl	45·5	27	72·5	1·87	74·6	40·0	32·5	28·4	53·0	24·3	105·7	105·6	+0·1
NaCl	23·7	27	50·7	2·04	58·5	28·7	22·0	19·3	54·2	24·3	97·8	97·7	+0·1
LiCl	13·1	27	40·1	1·575	42·5	27·0	13·1	11·5	58·0	24·3	93·8	93·8	±
HNO_3	12·0	49	61·0	1·53	63·0	41·2	19·8	17·3	1·0	26·0	44·3	41·5	+2·8
KNO_3	45·5	49	94·5	2·06	101·2	49·1	45·4	39·7	53·0	26·0	118·7	119·5	−0·8
$NaNO_3$	23·7	49	72·7	2·25	85·0	37·8	34·9	30·5	54·2	26·0	110·7	111·3	−0·6
$LiNO_3$	13·1	49	62·1	2·33	69·0	29·6	32·5	28·4	58·0	26·0	112·4	111·6	+0·8
HIO_3	12·0	62	74·0	4·63	176·0	38·0	36·0	31·5	1·0	25·0	57·5	58·0	−0·5
KIO_3	45·5	62	107·5	3·98	214·2	53·8	53·7	47·0	53·0	25·0	125·0	124·5	+0·5
KBr	45·5	26	71·5	2·7	119·1	44·1	27·4	24·0	53·0	17·7	94·7	95·3	−0·6
NaBr	23·7	26	49·7	3·08	103·0	33·4	16·3	14·3	54·2	17·7	86·2	85·8	+0·4
KI	45·5	26	71·5	3·07	166·2	54·1	17·4	15·2	53·0	9·5	77·7	80·1	−2·4
NaI	23·7	26	49·7	3·45	150·0	43·5	6·2	5·4	54·2	9·5	69·1	69·1	±
			H.	K.	Na.	Li.	NO_3.	IO_3.	Cl.	Br.	I.		
Values of V			12	45·5	23·7	13·1	49·0	62	27·0	26·0	26·0		
Values of H			1	53·0	54·2	58·0	26·0	25	24·3	17·7	9·5		

$$\Sigma = 0{\cdot}875\,\delta V + H_1 + H_2.$$

sum in the column headed Σ. The column headed "Diff." shows the differences between the observed and calculated heats of formation.

The principle which is involved in the relationship which thus comes to light is probably capable of wider application, but data for extending the generalisation are very difficult to obtain. At the suggestion of Prof. Sir J. Larmor data have been collected for another group. They are set out in Table II. The errors between observed and calculated values are about twice as great as in the first group, but the heats of formation of the bivalent salts are also about twice as great. Within the area of both these groups we can say that the heat of formation due to the combination of one of the electro-positive atoms with one of the electro-negative atoms or radicles is the sum of three components, two of which are constants belonging to the several combining atoms or radicles, and the other of which is approximately 0·875 δV, where δV is the contraction which takes place on combination.

The last component possesses great interest in connection with the theory of the compressibility of the atom. It appears probable that the component represents the change of internal energy due to the contraction of the atoms on combination.

Let us conceive the corpuscles of a free or uncombined atom as vibrating in a certain maximum space with a maximum average amplitude at a given temperature, the volume of the atom being determined by an equilibrium between attractive forces, which tend to approximate the corpuscles and to reduce the volume, and the energy of motion of the corpuscles, which tends to increase the volume. If we suppose such an atom to contract or to be compressed isothermally, the internal kinetic energy would be diminished, owing to the reduction of the amplitude of the corpuscular vibrations with reduction of volume, and the internal potential energy would be diminished, owing to the approximation of mutually attractive corpuscles. This reduction of internal energy appears to be expressed by, or at all events included in, the component 0·875 δV, which would thus represent the heat so developed. This, in the case of KCl, amounts to more than a quarter of the total heat of formation, and in the case of the nitrates and iodates to a still larger fraction. We have spoken of a reduction of internal energy due to compression, but it must be observed that in the cases of HCl and ZnI_2, to which the law also extends, there is an increase of atomic volume on combination, and a resulting increase of internal energy.

We may now apply the result obtained as regards δV to the consideration of the heats of formation of ions. The compression of the atoms in the ionic state is even greater than in the solid state, as we may see from the values of

Table II.—Components of Heats of Formation of Solid Salts with Bivalent Bases.

	V_1.	$2V_2$.	V_1+2V_2.	ρ.	W.	W/ρ.	δV.	$\frac{7}{8}\delta V$.	H_1.	$2H_2$.	Σ.	H.F.	Diff.
$CaCl_2$ …………	25·3	54	79·3	2·205	111·1	50·4	28·9	25·3	93·2	48·6	167·1	169·8	−2·7
$SrCl_2$ …………	35·0	54	89·0	2·96	158·6	53·6	35·4	31·0	102·7	48·6	182·3	184·6	−2·3
$BaCl_2$ …………	36·0	54	90·0	3·75	208·4	55·5	34·5	30·2	118·1	48·6	196·9	194·7	+2·2
$ZnCl_2$ …………	9·5	54	63·5	2·753	136·4	49·5	14·0	12·3	38·0	48·6	98·9	97·2	+1·7
$CdCl_2$ …………	13·0	54	67·0	3·655	183·4	50·2	16·8	14·7	31·2	48·6	94·5	93·2	+1·3
$CaBr_2$ …………	25·3	52	77·3	4·794	200·1	60·3	17·0	14·9	93·2	35·4	143·5	140·9	+2·6
$SrBr_2$ …………	35·0	52	87·0	3·985	247·6	62·1	24·9	21·8	102·7	35·4	159·9	157·7	+2·2
$BaBr_2$ …………	36·0	52	88·0	4·23	297·4	70·3	17·7	15·5	118·1	35·4	169·0	170·0	−1·0
$ZnBr_2$ …………	9·5	52	61·5	3·643	225·4	61·9	−0·4	−0·4	38·0	35·4	73·0	75·9	−2·9
$CdBr_2$ …………	13·0	52	65·0	4·794	272·4	56·8	8·2	7·2	31·2	35·4	73·8	75·2	−1·4
ZnI_2 …………	9·5	52	61·5	4·696	319·4	68·0	−6·5	−5·7	38·0	19·0	51·3	49·2	+2·1
CdI_2 …………	13·0	52	65·0	5·644	366·4	64·9	0·1	0·1	31·2	19·0	50·3	48·8	+1·5
Values of H …………				Ca. 93·2	Sr. 102·7	Ba. 118·1	Zn. 38	Cd. 31·2	Cl. 24·3	Br. 17·7	I. 9·5		

$$\Sigma = \tfrac{7}{8}\delta V + H_1 + 2H_2.$$

δV set out below, which are deduced from the values of EV_0 obtained in Section 7.

	KCl.	NaCl.	LiCl.
Solid state, δV	32·5	22·0	13·1
Ionic state, δV	42·7	29·9	18·7

This is probably due to the superiority of the attractive forces which come into play as between the atoms and water, over the mutual forces between the atoms themselves of the solid solute.

The heats of formation of the solid salts, which are in the order of their atomic weights and volumes, being

KCl.	NaCl.	LiCl.
105·6	97·7	93·8

may be regarded as periodic functions.

On the other hand, the heats of ionisation appear to be irregular, being

101·2 96·5 102·2

It seems clear that the heat component due to atomic compression, which probably expresses the reduction of the internal energy of the atom due to the approximation of its corpuscles, should equally be a component of the heat of ionisation. The application of this consideration at once regularises the heats of ionisation.

	KCl.	NaCl.	LiCl.
Heats of ionisation	101·2	96·5	102·2
0·875 δV	37·4	26·2	16·4
Remainder	63·8	70·3	85·8

If $n = 9, 13, 21$, respectively be the numbers of water molecules combined with the solute (see the last section of this paper), and if we attribute to each molecule of combined water a calorific constant 1·85, we may express the heats of ionisation of the three salts by one formula

$$\text{Heat of ionisation} = 0{\cdot}875\,\delta V + 1{\cdot}85\,n + 46{\cdot}6.$$

It will be noticed that in this scheme the idiosyncrasies of the ions K, Na, Li have disappeared except so far as they affect contraction and water combination, no place having been found for their individual calorific constants H_1 and H_2, as to whose values it may be observed that they are so

near to one another that they would not throw out by much the constant 46·6, which is included in the above scheme. Moreover, we have not included anything for the water contraction, except that its effect will be approximately brought out in the water calorific constant 1·85 per molecule. We will, therefore, now include all these elements in the scheme and see how the matter stands.

It appears highly probable that the heat component 0·875 δV, which represents the heat correlated with the contraction of the atoms, must also be applied to the contraction of the water. We can work out this contraction from the figures in the last section of the paper, which give

	KCl.	NaCl.	LiCl.
Total contraction δV of combined water......	3·518	5·457	4·880
And therefore for water, 0·875 δV	3·1	4·8	4·3

If we now include this item and also the calorific constants for the atoms, we find that on this basis the calorific constant for the water molecule works out at 1·3 (a figure which agrees approximately with the figures later deduced from the hydration of H_2SO_4), and there is a negative heat component which is approximately 29.

The whole scheme is then as follows:—

Table III.—Components of Heats of Ionisation.

	KCl.	NaCl.	LiCl.
0·875 δV (solute)	37·4	26·2	16·4
0·875 δV (water)	3·1	4·8	4·3
$H_1 + H_2$	77·3	78·5	82·3
1·3n	11·7	16·9	27·6
Negative constant	−29·0	−29·0	−29·0
Sum of components ...	100·5	97·4	101·6
Heats of ionisation	101·2	96·5	102·2
Difference	−0·7	+0·9	−0·6

Thus within the narrow margin shown by the differences the three heats of ionisation are given by

$$\Sigma\, 0{\cdot}875\, \delta V + \Sigma H + 1{\cdot}3\, n - 29.$$

On the whole, this must be regarded as the most probable scheme, and it has the advantage of bringing heats of formation of solid salts and ionised salts under one general law, when it is noted that the number 1·3 for the

water molecule is a calorific constant of precisely the same kind as those belonging to the atoms and radicles.

It should be noted that the appearance of a negative constant is necessary, since the heats of ionisation are the sum of not only positive but negative elements.

It might be thought, at first sight, that to attribute a calorific constant to water molecules when they enter into combination in different numbers with different salts would be inconsistent with the well-known generalisation of Thomsen that the addition of each successive molecule of water adds a diminished quantity to the heat of formation. This, however, is not necessarily the case. First, it must be noted that we have only dealt with the limiting case of practically complete ionisation. Then, too, the contraction δV for each successive molecule of water is probably less.

It must also be remembered that Thomsen's figures refer to the heat per molecule of water added, and that only a portion of this enters into actual combination. We may give an example of this by considering the heats due to the mixture of H_2SO_4 with 1, 2, and 3 molecules of water. The researches of Mendeléeff, Pickering and others make it probable that up to two molecules of water nearly the whole of the added water is in chemical combination with the acid. The heat of dilution law which our general law yields if the whole water enters into combination is

$$F = 0{\cdot}875\,\delta V + nH_w,$$

where n is the number of molecules of water in combination with the solute, and δV the contraction which takes place on addition of the water. We may take Mendeléeff's density data* and Thomsen's data for the heats of dilution F. Mendeléeff's figures are for 15° C. and Thomsen's data for 18° C., which will produce a small inaccuracy.

Table IV.—Heats of Dilution of $H_2SO_4 + nH_2O$.

n.	ρ_{15}.	δV.	F.	$0{\cdot}875\,\delta V$.	$F - 0{\cdot}875\,\delta V$.	H_w.
0	1·8372					
1	1·7772	6·08	6·38	5·32	1·06	1·06
2	1·6500	8·16	9·42	7·14	2·28	1·14
3	1·5501	9·33	11·14	8·16	2·98	0·99

The last column shows the value of H_w which results from these figures on the assumption that the whole of the water is in combination with the acid. Thus up to $n = 2$ a value for H_w is yielded which is very nearly equal to the value 1·3 deduced from the ions of the three salts above mentioned. For

* 'Principles of Chemistry,' Ed. 1905, vol. 2, p. 271.

three molecules the value of H_w falls off and still more as n increases, indicating that after the addition of two molecules of water, further additions only combine in part with the acid, a proportion of the water remaining as free water. In fact, the low values we get for H_w for the first two molecules of water may indicate that the whole of the water is not combined.

We may now summarise some of the results which this investigation tends to establish within the area which has been considered.

(1) The heats of formation both of the solid, liquid, and ionic molecules considered have a component $0·875\,\delta V$ depending upon the total contraction of the combining atoms and radicles and water molecules.

(2) These heats of formation have also components which are calorific constants for the various atoms and radicles and also for the combining water molecules.

(3) The theory of the compressibility of the atom is in accord with these results and interprets our component $0·875\,\delta V$ as the heat evolution due to the reduction of the internal energy of the atom owing to the contraction due to combination.

(4) In the process of ionisation, the ionic nuclei, which are reduced in size, may be regarded as in a state of chemical combination with their attached water molecules, such combination yielding the energy required for dissociating the solid salt, together with a surplus.

3. *Experimental Work. Density and Viscosity of LiCl Solutions.*—To determine solution volumes in dilute solutions with sufficient accuracy for our purpose, densities accurate within a unit in the fifth place of decimals are required. For the present determinations were used a pair of pyknometers of the kind formerly described* of a capacity of 300 to 400 c.c. The most important determinations were made in duplicate and in some cases repeated. The figures are given in the following table :—

Table V.—Density Determinations of LiCl Solutions at 18° C.

m.	First series.	Second series.		Value taken.	V_s.
		Pyk. I.	Pyk. II.		
1	1·02286	1·022928	1·022922	1·02292	0·4294
$\frac{1}{2}$	1·01100			1·01100	0·4190
$\frac{1}{4}$	1·00494			1·00494	0·4087
$\frac{1}{8}$	1·00184			1·00184	0·4011
$\frac{1}{16}$	1·00028	1·000254 1·000257	1·000250 1·000255	1·000265	0·396
$\frac{1}{32}$	0·99950	0·999473 0·999466	0·999466 0·999457	0·99947	0·3926
$\frac{1}{64}$	0·99909			0·99909	

* 'Trans. Chem. Soc.,' 1908, vol. 93, p. 679.

The values of the solution volume V, calculated from the densities are given in the last column.

The viscosities of the LiCl solutions were determined with a viscosimeter of the type described in a former paper.* The observations were made in duplicate. The results are given in the following table, together with the equivalent viscosity increment. The viscosity of water at 18° C. is taken as the unit:—

Table VI.—Viscosities of LiCl Solutions at 18° C.

m.	η.	$\frac{\eta-1}{m}$
1	1·1497	0·1497
$\frac{1}{2}$	1·0761	0·1522
$\frac{1}{4}$	1·0392	0·1568
$\frac{1}{8}$	1·0207	0·1656
$\frac{1}{16}$	1·0116	0·1856
$\frac{1}{32}$	1·0071	0·2272
$\frac{1}{64}$	1·0045	

From $m = 1$ to $m = 1/16$ a straight line law expresses the viscosity with good accuracy for interpolation as follows:—

$$\eta = 1{\cdot}0024 + 0{\cdot}1473\, m.$$

Beyond $m = 1/16$, the values at the points required for our calculations can be obtained by setting out the values of the equivalent viscosity increment upon a curve. The required values are as follows:—

m.	η.
0·0005	1·0002
0·001	1·0003
0·005	1·0014
0·01	1·0026
0·05	1·0095
0·10	1·0170

Grüneisen† determined the viscosity of LiCl solutions, but only at two points. His values, compared with those above, are as follows:—

m.	Values above.	Grüneisen.
1·0	1·1497	1·1498
0·1	1·0171	1·0161

* "Ionic Sizes I," p. 304.

† 'Wiss. Abhand. der Phys. Tech. Reichsanstalt,' 1905, vol. 4, p. 246.

It is considered that the present values, based on a complete series, are preferable to those of Grüneisen.

4. *The Empirical Volume Equations.*—For the method of deduction of the ionic volumes reference must be made to the former papers. For obtaining the true values of α from the Van't Hoff equation, the following values of C are taken :—

	KCl.	NaCl.	LiCl.
$C =$	0·505	0·520	0·531

The ionisations which result from the use of these constants may be compared with those which result from taking the ordinary $\alpha = \lambda/\lambda_\infty$ at the concentration $m = 0{\cdot}001$. The values resulting from these values of C are :—

	KCl.	NaCl.	LiCl.
$\alpha =$	0·9765	0·9753	0·9744

whilst the other values are

	KCl.	NaCl.	LiCl.
$\lambda/\lambda_\infty =$	0·9788	0·9771	0·9761

The latter values, which neglect variation of viscosity and ionic size, are, as they should be, somewhat higher than our values, but the relative ionisations remain about the same.

As a slightly different value of the constant for NaCl is now taken, the figures for NaCl have been recalculated. The required empirical relation between solution volumes and ionic volumes for LiCl, calculated as in the former papers, is

$$V_s = 0{\cdot}5112 - 0{\cdot}004094\, I_V.$$

It is useful as a test of our values for the ionic volumes to see what values for the densities are obtained from the ionic volumes. Density may be expressed in terms of solution volumes as

$$\rho = \rho_0 + \frac{m}{1000}(E - \rho_0 E V_s),$$

where $\rho_0 = 0{\cdot}99866$, the density of water at 18° C., and $E = 42{\cdot}48$, the molecular weight of LiCl.* Substituting these values and expressing V_s in terms of I_V, we have for the density

$$\rho = 0{\cdot}99866 + m(0{\cdot}02079 + 0{\cdot}0001737\, I_V).$$

It will be noticed that there are in this equation only two independent constants, the values of I_V having been obtained entirely without reference to the densities. The calculated and observed densities are set out in the table.

* In this paper the old molecular weights are taken, as Kohlrausch's values of λ were used on these figures.

Table VII.—Observed and Calculated Densities of LiCl at 18° C.

m.	I_V.	ρ observed.	ρ calculated.	Difference.
1	19·11	1·02292	1·02277	−15
$\frac{1}{2}$	22·51	1·01100	1·01101	+ 1
$\frac{1}{4}$	25·05	1·00494	1·00494	±
$\frac{1}{8}$	26·84	1·00184	1·00184	±
$\frac{1}{16}$	28·06	1·00026	1·00026	±
$\frac{1}{32}$	28·86	0·99947	0·99947	±
$\frac{1}{64}$	29·39	0·99909	0·99907	− 2

We may repeat an observation made in a former paper. The ionic volumes are obtained only from the sizes of the ions, being based on conductivity measurements which take no account of un-ionised molecules. The fact that the densities can be accurately calculated from the ionic volumes indicates that the un-ionised molecules follow approximately the same volume law as if they consisted of two ions joined together. It is important to bear this in mind, as it enables us to use the ionic volumes for deriving the total amount of water combination both for ionised and un-ionised molecules.

The complete results from this and the former papers are as follows :—

Hydration Numbers B.

$$B_{KCl} = 3{\cdot}33, \quad B_{NaCl} = 3{\cdot}2, \quad B_{LiCl} = 3{\cdot}08,$$

$$B_{Cl} = 3{\cdot}5, \quad B_K = 3{\cdot}16, \quad B_{Na} = 2{\cdot}75, \quad B_{Li} = 2{\cdot}26.$$

Empirical Relations between I_V and V_s.

KCl .... $V_s = 0{\cdot}408 - 0{\cdot}0075\,I_V$.

NaCl .... $V_s = 0{\cdot}3647 - 0{\cdot}00655\,I_V$.

LiCl .... $V_s = 0{\cdot}5112 - 0{\cdot}004094\,I_V$.

The molecular solution volumes are obtained by multiplication by the equivalent weights, which are (old atomic weights)—

	KCl.	NaCl.	LiCl
E =	74·6	58·5	42·48.

These lead to the empirical volume relations in the form in which they are required for use :—

KCl .... $EV_s = 30{\cdot}44 - 0{\cdot}560\,I^V$.

NaCl .... $EV_s = 21{\cdot}33 - 0{\cdot}383\,I_V$.

LiCl .... $EV_s = 21{\cdot}72 - 0{\cdot}1739\,I_V$.

These equations are of the form

$$EV_s = a - bI_V,$$

the constants a and b for each salt being as shown.

5. *Comparative Values of Ionic Volumes.*—In the former paper* the application of Stokes' theorem, on the assumption that the ions were spherical and had approximately the same coefficient of friction, led to the relationship $r = G/v\eta$, where r is the radius of the ion, v its true mobility, η the viscosity of the solution, and G was taken as a constant for monovalent ions and the value unity was given to it. The examination of this relationship over a larger group soon showed that this could only be regarded as a first approximation, and it became clear that variations of ionic shape and of friction had to be reckoned with, so that G must be regarded as varying from ion to ion. Moreover, in seeking for a factor for reducing the arbitrary ionic volume units to the ordinary volume unit, it already appeared† that a slightly different factor would have to be taken for KCl and NaCl. The factor γ which was used for converting ionic volume units to litres was obtained from a consideration of the relative viscosities and was taken to be 0·32 for KCl and 0·30 for NaCl. A much greater difference in the factor γ was found to be necessary when LiCl was brought into consideration, and the deduction of the factor from the viscosities, in any case a difficult matter, was found to be still more difficult. It therefore became necessary to find a better method for evaluating γ. Now in working from the factors deduced from the viscosities it was found‡ that, both in the case of KCl and NaCl, we were led to the result that the effective molecular freezing-point depression, over a certain range of concentration, came out as a constant when reckoned upon the free water in the solution, that is, after deducting from the total water the amount of combined water calculated from the ionic volumes. In the present paper this is taken as the starting point for the determination of γ. A new and more convenient empirical relation between ionic volume and freezing-point depression enables the factors to be worked out upon a systematic basis. This relation is of the form

$$\frac{1}{D} = p - qN(I_V - K),$$

where D is the effective molecular freezing-point depression, N is the number of gramme-molecules of solute per 1000 grm. water, I_V is the ionic volume reckoned in the old units, and K is the volume of the ionic nuclei in the same units, p and q being constants. By the use of this empirical relation in combination with that between ionic volume and solution volume it is possible to evaluate γ and to obtain the volumes both of the ions and of the ionic nuclei. One theoretical defect in this process must not be overlooked.

* "Ionic Sizes II," p. 155.
† "Ionic Sizes II," p. 139.
‡ "Ionic Sizes II," p. 149.

This is that we are using ionic volumes based on conductivities measured at 18° C. as applicable to the solutions in the neighbourhood of the freezing point. To make our deductions strictly accurate, the ionic volumes should be based on conductivities also measured in the neighbourhood of the freezing point. But no sufficiently accurate data of this kind are in existence. The general character of the deductions of this paper will not be seriously modified by this defect.

It should be remembered that though a different factor γ is required for each salt to make the ionic volumes derived from the mobilities comparable as between the different salts, yet for any given salt the ionic volumes are strictly comparable through a certain range of concentration. Each set of ionic volumes, calculated as in the former papers from conductivity and viscosity data, must be considered as being given in its own arbitrary unit, the factor γ in each case reducing the arbitrary unit to ordinary units.

It should be noted that though we use the separate radions r_1 and r_2 of the positive and negative ions to arrive at the joint ionic volume of the solute $(r_1^3+r_2^3)\times 10^6$, our factor γ, being applied to the joint volumes, cannot be used to obtain the absolute values of the radions. These are not wanted for our present purpose, but to indicate that r_1 and r_2 require different factors to reduce them to absolute values it is better to term r_1 and r_2 the "mobility radions."

6. *Analytical Treatment of the Empirical Equations.*—Before we are in a position to evaluate the required constants of the new empirical relation

$$\frac{1}{D} = p - q\mathrm{N}(\mathrm{I_V} - \mathrm{K}),$$

it is necessary to consider its physical meaning in combination with that of the other empirical relation

$$\mathrm{EV}_s = a - b\mathrm{I_V}.$$

It will be convenient at this stage to collect together the symbols used in a tabulated form for reference.

Symbols Used.

V_s = Solution volume of 1 grm. of solute.

V_0 = Volume which 1 grm. of solute occupies in solution.

E = Weight of 1 gramme-molecule of solute.

ϵ = Weight of 1 gramme-molecule of water.

ρ_u = Density of free or uncombined water.

ρ_c = Average density of water which is in combination with the solute.

ϵ/ρ_u = Volume of 1 gramme-molecule of free water.

ϵ/ρ_c = Volume of 1 gramme-molecule of combined water.

$\zeta = \epsilon\left(\frac{1}{\rho_u} - \frac{1}{\rho_c}\right)$ = contraction which 1 gramme-molecule of water undergoes in combination.

n = Number of molecules of water combined with 1 molecule of solute.

I_V = Ionic volume of a gramme-molecule of solute with its combined water.

γ = Factor necessary to reduce ionic volume units to litres, so that

$1000\,\gamma I_V$ = Volume of 1 gramme-molecule of hydrated solute in cubic centimetres.

α = Coefficient of ionisation.

Δ = Freezing-point depression in degrees Centigrade of a solution containing N gramme-molecules of solute to 1000 grm. water.

$D = \frac{\Delta}{N(1+\alpha)}$ = effective molecular depression of the freezing point.

K = Volume of 1 gramme-molecule of solute in ionic units, so that

$EV_0 = 1000\,\gamma K$.

w = Weight of uncombined water in 1000 grm. of total water.

N = Molecules of solute to 1000 grm. water.

We found formerly* that the E.M.D., when reckoned upon the free water of the solution only, came out as a constant. The E.M.D. is

$$D = \frac{\Delta}{N(1+\alpha)},$$

when this is reckoned upon the total water. We shall still keep D to express this fraction. The fact that the E.M.D. when reckoned upon the free water is a constant will then be expressed by

$$\frac{Dw}{1000} = F, \tag{1}$$

where F is a constant, and is equal to 1·86, or whatever number we decide to adopt as best for the limiting value of the E.M.D.

The volume of water combined with 1 gramme-molecule of solute is $I_V - K$, where K is the volume of the ionic nuclei. If γ is the factor required to reduce ionic volumes to litres and ρ_c is the average density of the combined water, the weight (in grammes) of water combined with 1 gramme-molecule of solute is

$$1000\,\gamma\rho_c(I_V - K), \quad \text{so that} \quad w = 1000 - 1000\,N\gamma\rho_c(I_V - K).$$

Hence equation (1) may be expressed as

$$\frac{1}{D} = \frac{1}{F} - \frac{N\gamma\rho_c}{F}(I_V - K). \tag{2}$$

* "Ionic Sizes II," p. 149.

Our empirical relation is

$$\frac{1}{D} = p - qN(I_V - K). \tag{3}$$

Hence we have $\quad p = 1/F \quad$ and $\quad q = \gamma\rho_c/F,$

and we thus get for the required value of γ

$$\gamma = \frac{q}{p\rho_c}. \tag{4}$$

But there is still an unknown quantity ρ_c, the density of the combined water, involved in this equation and an unknown quantity K is required for the deduction of p and q. We can obtain these by a concurrent consideration of the other set of empirical relations

$$EV_s = a - bI_V. \tag{5}$$

To interpret this equation we must remember that EV_s, the solution volume of a molecule of solute, is the volume which the molecule of solute occupies in solution less the contraction of the water which combines with the solute, that is to say,

$$EV_s = EV_0 - n\zeta, \tag{6}$$

where V_0 is the volume which 1 grm. of solute occupies in the solution, ζ is the average contraction which 1 molecule of water undergoes in combination with the solute, and n is the number of molecules of water combined with 1 molecule of solute.

It must further be noted that the volume of 1 molecule of the hydrated solute, that is of 1 molecule of the ions and partly ionised molecules, is the volume which 1 molecule of solute occupies in solution *plus* the volume of the combined water, that is to say,

$$1000\gamma I_V = EV_0 + \frac{n\epsilon}{\rho_c}, \tag{7}$$

where ϵ is the weight of a molecule of water.

By elimination of n between (6) and (7) and noting that

$$\frac{\zeta\rho_c}{\epsilon} = \frac{\rho_c}{\rho_u} - 1,$$

where ρ_u is the density of the uncombined water, we get

$$EV_s = EV_0\frac{\rho_c}{\rho_u} - 1000\gamma\left(\frac{\rho_c}{\rho_u} - 1\right)I_V. \tag{8}$$

If we assume that at high dilutions ρ_c, the density of the combined water, and ρ_u, the density of the free water, are constants we may now compare our empirical equation (5) with equation (8), and equate coefficients. But it is likely that there may be a change in the density both of the free water and

the combined water in passing from high to low dilutions, and this limitation must, therefore, be borne in mind. Equating coefficients we get

$$a = \mathrm{EV}_0\frac{\rho_c}{\rho_u}, \tag{9}$$

$$b = 1000\gamma\left(\frac{\rho_c}{\rho_u}-1\right). \tag{10}$$

Now K is the volume of the ionic nuclei in the same units as I_V, and, therefore, $\mathrm{EV}_0 = 1000\gamma\mathrm{K}$. Hence from (9) and (10) we get

$$\mathrm{K} = \frac{a}{b}\cdot\frac{\rho_c-\rho_u}{\rho_c}. \tag{11}$$

From (4) and (10), by eliminating γ, we get

$$b = \frac{1000q}{p\rho_c}\left(\frac{\rho_c-\rho_u}{\rho_u}\right).$$

Whence also

$$\mathrm{K} = \frac{pa\rho_u}{1000q}. \tag{12}$$

K is thus expressed in terms of the constants of the empirical equations.

Also from (4) and (10) by eliminating ρ_c we get

$$\gamma = \frac{q}{p\rho_u}-\frac{b}{1000}, \tag{13}$$

and from (4), (9), and (13)

$$\mathrm{EV}_0 = a-\frac{pab\rho_u}{1000q}. \tag{14}$$

EV_0 is thus expressed in terms of the constants. By reason of (12) the last equation may be written in the interesting form

$$\mathrm{EV}_0 = a-b\mathrm{K}. \tag{15}$$

Finally, the density of the combined water is given by (9), which may be written

$$\rho_c = \frac{a\rho_u}{\mathrm{EV}_0}. \tag{16}$$

For the simple calculation of q from the experimental data we obtain from equations (3) and (12) the relation

$$q = \frac{1}{\mathrm{I_V}}\left[\frac{1}{\mathrm{N}}\left(p-\frac{1}{\mathrm{D}}\right)+\frac{pa\rho_u}{1000}\right]. \tag{17}$$

It will be noticed that we have treated ρ_c and ρ_u as if our conductivity data were taken at the same temperature as the freezing-point data. This may in some equations produce an error of nearly two parts per thousand, but the error produced on the value of q is inappreciable. It should also

be noticed that by treating ρ_c and ρ_u as constants in the region of high dilution we bring out K as a constant. This would introduce a small error at low dilution, as K must probably be larger at such dilutions, owing to the reduced pressure on the nuclei when the ions are smaller and the water combination is less. We have also neglected the difference in the value of K as between 0° C. and 18° C.

7. *The Empirical Relation between Freezing-Point Depression and Ionic Volume, and Deduction of Constants.*—We are now in a position to obtain the empirical relations between freezing-point depression and ionic volume for the three salts under consideration. Let us first take the identical set of figures set out in the former paper* for KCl. These were there shown to lead to the relation $D = 1{\cdot}86 + c\delta I_V$ within the limits of experimental error. They equally lead to the new relation

$$\frac{1}{D} = p - qN(I_V - K)$$

within the same limits. The choice of the new relation instead of the old one is determined by the fact that it admits of a precise theoretical interpretation as was shown in the preceding section.

In the following table, in the first, second, third, and fourth columns are set out the same figures as were formerly given for KCl. The values for the molecular depression of the freezing point Δ/N are those given by Jahn.†

The figures given for the calculated values of 1/D are obtained by taking

$$p = 0{\cdot}534, \qquad q = 0{\cdot}0138, \qquad K = 1{\cdot}2.$$

Table VIII.—Empirical Relation between Freezing-point Depression and Ionic Volume for KCl.

N.	I_V.	α.	Δ/N.	$\frac{1}{D} = \frac{N(1+\alpha)}{\Delta}$.	$I_V - K$.	$qN(I_V - K)$.	1/D calc.	Diff.
0·3395	5·297	0·727	3·337	0·518	4·097	0·0192	0·515	−3
0·3377			3·344	0·515		0·0191	0·515	±
0·259	5·568	0·749	3·37	0·519	4·368	0·0156	0·518	−1
0·201	5·794	0·769	3·385	0·523	4·594	0·0127	0·521	−2
0·151	6·021	0·790	3·41	0·524	4·821	0·0121	0·522	−2
0·100	6·289	0·819	3·472	0·524	5·089	0·0070	0·527	+3
			3·457	0·526			0·527	+1
0·076	6·448	0·837	3·485	0·527	5·248	0·0055	0·529	+2
0·054	6·626	0·863	3·50	0·532	5·426	0·0038	0·530	−2
0·0378	6·783	0·878	3·55	0·529	5·533	0·0029	0·531	+2
0·02552	6·881	0·896	3·547	0·535	5·681	0·0020	0·532	−3
0·02527			3·562	0·532		0·0020	0·532	±

* "Ionic Sizes II," p. 143.

† 'Zeit. Phys. Chem.,' 1904, vol. 50, p. 136.

If we look at the values of $1/D$ derived from Jahn's duplicate experimental values for Δ/N, we see that the differences on our calculated values of $1/D$ are of the same order as Jahn's experimental differences, and we may therefore say without doubt that the new empirical relation is established within the limits of experimental error. At the lowest concentration, which is the most important for determining the limiting value of $1/D$, Jahn's results give a difference of 0·003 on $1/D$. But such experimental differences at low concentration cannot be avoided, and, as a consequence, we find that Jahn's figures for the three salts KCl, NaCl, LiCl, yield three different values for the constant p, which should theoretically be the same for each.

It seems clear that these differences in the value of p, which is the limiting value of $1/D$ at infinite dilution, can only be due to experimental errors, and we shall, therefore, take a fixed value for p which is the same in all three cases. The reciprocal of the value 0·534 which is yielded by the above figures is 1·872. This is a higher value than that which is usually accepted. Bedford's figures* seem to be the most recent and the most reliable. The highest figures which he obtained for the molecular depression of the freezing point with KCl solutions were 3·736 and 3·734, corresponding to effective molecular depressions of 1·868 and 1·867. We shall assume as the basis of our calculation 1·867 as the right figure, instead of 1·874. This gives the value of our constant $p = 1/1{\cdot}867 = 0{\cdot}5355$, instead of 0·534. Taking this value of p we might deduce from Jahn's figures for each salt a value of q for the salt which would be the mean value yielded by all the figures. Since, however, the probable error in the value of Δ/N given by any particular observation is inversely proportional to N^2 we shall deduce the value of q from the mean of the two highest concentrations given in each case by Jahn. As we are dealing with a straight line law this will be likely to give us the best values.

The figures which Jahn gives for these concentrations are as follows:—

Table IX.—Jahn's Values for Depression of Freezing Point.

	N.	Δ.	Δ/N.
KCl	0·3395	1·1320	3·337
	0·3377	1·1292	3·344
NaCl	0·3022	1·0279	3·401
	0·2998	1·0207	3·404
LiCl	0·2936	1·0370	3·530
	0·2939	1·0389	3·535

Using the values of the hydration numbers B and ionisation constants C before given we arrive at the following figures by taking the mean of each pair of observations.

* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 454.

	N.	$h = \frac{55 \cdot 506}{N}$.*	Log h.	a.	I_v.
KCl.........	0·3386	163·9	2·21458	0·7244	5·298
NaCl	0·3010	184·4	2·26576	0·7257	12·105
LiCl.........	0·29385	188·9	2·27623	0·7211	24·546

* h is the number of molecules of water per gramme-molecule of solute.

From these figures, taking $p = 0{\cdot}5355$, we arrive at the values for q and K which are given in the following table:—

Table X.—Values of the Constants q and K.

	Δ/N.	1/D.	q.	K.
KCl......	3·3405	0·5162	0·01383	1·176
NaCl ...	3·4025	0·5072	0·00871	1·310
LiCl......	3·5325	0·4872	0·00717	1·620

The values of q are easily obtained by the use of equation (17), taking the given data and putting $p = 0{\cdot}5355$, $\rho_w = 0{\cdot}99866$, and taking the value of a furnished by the empirical volume relation.

Our complete table of the constants of the empirical equations and of the values deduced from them by means of equations (4), (12), (13), (14), (15), and (16) is as follows:—

Table XI.—Constants Derived from the Empirical Equations.

	a.	b.	p.	q.	K.	EV_0.	ρ_c.	$1000\,\gamma$.
KCl......	30·44	0·560	0·5355	0·01383	1·176	29·78	1·0208	25·30
NaCl ...	21·33	0·383	0·5355	0·00871	1·310	20·83	1·0225	15·92
LiCl ...	21·72	0·1739	0·5355	0·00717	1·620	21·44	1·0117	13·25

8. *Application to Ionic Volumes at Infinite Dilution.*—We are now in a position to complete the data required, in order to arrive at the analysis of the ionic heats which is contained in Section 2 of this paper. For this purpose it is only necessary to apply the figures obtained to deduce approximately the number of molecules of water combined with each pair of ions. The total volume of a gramme-molecule of ions in cubic centimetres is $1000\,\gamma I_V$. From this we must deduct the volume of the ionic nuclei to get the volume of the combined water, and multiply by the mean density of this water to get

the weight. Hence the weight of water combined with a gramme-molecule of ions of the solute at infinite dilution is

$$\rho_c(1000\gamma I_V - EV_0).$$

Using the data given above the weights of combined water deduced are as follows:—

KCl.	NaCl.	LiCl.
157·1	233·9	384·6

which expressed in molecules of water are

	KCl.	NaCl.	LiCl.
$n =$	8·9	13	21·3

These numbers should be integers at infinite dilution, and taking the nearest integers we get for the molecules of water combined with the pairs of ions at infinite dilution,

KCl.	NaCl.	LiCl.
9	13	21

It has, of course, been observed that our analysis has not given us any means of separating the volumes of the several ions, or of the amounts of their separate water combination. Our factor γ is a factor which deals with the sum of the ionic volumes, and our quantity EV_0 is the sum of the volumes of the nuclei. But having regard to the mobilities of K and Cl and to the transference numbers, we may reasonably conclude that the K and Cl ions are of nearly equal size.

If we took the Cl ion to be combined with five molecules of water, we should have for the water combination of the other ions

	K.	Na.	Li.
$n =$	4	8	16

This is a very attractive looking series and there is something to be said for it. Let us compare certain corresponding properties of the K and Cl atoms and ions—

	K.	Cl.
Mobilities	64·6	65·4
Atomic volumes	45·0	27·0
Compressibilities	31·5	95·0

Now the joint contracted volume in the ionic state is 30. This is 5/12ths of the original joint volume 72. If the compressibilities were equal and the internal pressures in the ions equal, the respective contracted volumes would be

$$18·7 + 11·3 = 30;$$

but, allowing for the difference in compressibility, they might be more nearly

$$25+5 = 30.$$

This would allow the Cl ion to have one more molecule of water than the K ion, and yet have a less volume and greater mobility.

Unfortunately, Washburn's transference experiments in order to determine the relative hydration* indicate that the numbers should be the other way, and that the K ion has one more molecule than the Cl ion, in which case the numbers for the separate ions yielded by our figures would be

	Cl.	K.	Na.	Li.
$n =$	4	5	9	17

Whether Washburn's method, which rests on the mixture with the solution of a non-electrolyte, such as sucrose or raffinose, is completely reliable is possibly open to some question. If the Cl ion be taken to be combined with four molecules of water, the figures which his experiments yield are

	Cl.	K.	Na.	Li.
$n =$	4	5·4	8·4	13·0

which may be compared with those above. His figures are only relative, as his method does not yield absolute results, and the figures are for concentrations of about 1·2 normal instead of infinite dilution.

The division of the combined water between the separated ions is a matter of great interest, but fortunately it is quite unnecessary for the main purpose of this paper, which was developed in the second section.

In conclusion, we may again refer to the fact that the precise figures depend, according to this method, on what is to be taken as the true value of the freezing-point constant. If the low value 1·845 be taken instead of the value 1·867, the figures come out as follows:—

	KCl.	NaCl.	LiCl.
$n =$	11	16	24

but the general results of the second section of this paper are not affected thereby, though the value of the calorific constant 1·3 for the water molecule in combination would be slightly altered.

* 'Technological Quarterly,' 1908, vol. 21, p. 288.

On the New Theory of Integration.

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(Received November 28, 1912,—Read January 16, 1913.)

§ 1. In a paper published in the 'Proceedings of the London Mathematical Society,'* addressed to persons already acquainted with Lebesgue integration, I endeavoured to show that the method of monotone sequences enabled us to recognise intuitively the extensibility to Lebesgue integration of results known to be true for Riemann integrals. For this purpose I naturally employed known results in the Theory of Sets of Points; and, of course, also pre-supposed the proofs of the classical theorems whose generalisation was in question.

In the present communication I propose to indicate briefly how the method of monotone sequences enables us to prove, at one and the same time, these theorems and their generalisations. For this purpose we have only to employ a slight modification of the procedure indicated in the paper cited; one which, however, avoids all reference to the Theory of Sets of Points,† and assumes no results whatever in the Theory of Integration.

A careful study of the classical treatment of the theory of the integration of a continuous function shows that it is based on two principles, which are, however, not explicitly alluded to:—

(1) The function whose integral is required is approached as limiting function by discontinuous functions, whose integrals are already known, being in fact synonymous, if there be only one independent variable, with the sum of a finite number of rectangular areas; these functions, which are constant in each of a finite number of stretches, by a natural and convenient choice of values at the points, necessarily finite in number, at which there is ambiguity, are, at our will, upper or lower semi-continuous functions.‡

(2) The mode in which the limiting function is approached is by means of monotone sequences of these functions, and it is shown that, whatever

* "On a New Method in the Theory of Integration," 'Lond. Math. Soc. Proc.,' 1910, Ser. 2, vol. 9, pp. 15–50.

† It is at the request of a distinguished mathematician of the older school that I have undertaken to explain the possibility of doing this. I hope that the novelties in the present account will be regarded as sufficiently justifying the publication of this communication.

‡ For the definition and properties of semi-continuous functions see my tract "On the Fundamental Theorems of the Differential Calculus," 'Camb. Univ. Press,' 1910, pp. 6, 7.

monotone sequence of functions of the elementary type in question be employed, the limit of their integrals is necessarily the same.

If we then turn to the work of Darboux, to whom, and not to Riemann, our theory in its most generalised form is chiefly indebted, we find that he tacitly replaces the discontinuous function of which he is desirous to define the integral by two functions, one a lower semi-continuous function not greater than the given function, and the other an upper semi-continuous function not less than the given function. To each of these functions he may be said to apply one half of the process employed in the classical theory in the case of a continuous function. The lower semi-continuous function is approached from below, and the upper semi-continuous function from above only. It follows, however, from the theory of such functions; and, in particular, from the fact that, if we divide an interval into a finite number of parts, and select a point in each part at which the function assumes its minimum value in that part—supposing it to be a lower semi-continuous function—or its maximum in that part—supposing it to be an upper semi-continuous function—and then subdivide each of the parts so obtained, and carry on the process indefinitely, the value of the function at every point is the unique limit of these minima, or maxima, respectively in its neighbourhood—it follows, I say, from this fact, that the upper and lower semi-continuous functions in question are actually the limits of the discontinuous functions approaching them. Moreover, the mode of approach is a monotone one; and, as Darboux virtually shows, the limit of the integrals of the auxiliary functions approaching from below, and the limit of the integrals of the auxiliary functions approaching from above, are each of them unique and independent of the particular auxiliary functions, of the types specified, chosen to approximate to the given function. These two limits are not, however, in general the same, and Darboux gives to them the names of *intégrale par défaut* and *intégrale par excès* respectively.

It lies in the nature of things to call these *intégrales par défaut et par excès* the integrals of the lower and upper semi-continuous functions respectively which the generating functions have as limits. Yet, as soon as we have done this, we have already taken a step into a domain which was closed to Riemann.

If further justification for this step is needed, it is easy to give it. The extension to unbounded functions of the theory of integration in its most successful form, as developed by de la Vallée Poussin, involved monotone sequences before the idea of Lebesgue integration had been mooted. On the other hand, if for a moment we turn to the Theory of Sets of Points, we shall find that the definition we have just given of the integral of an

upper semi-continuous function, for example, corresponds precisely, in the Theory of Sets of Points, to the convention by which we attach to a *closed* set of points a content. Now, even Riemann and his disciples have, implicitly or explicitly, always admitted the logical character of this convention. The identity in question is evident, if we reflect that the function which is unity at every point of a closed set of points in the interval of integration, and zero elsewhere (*i.e.* in the complementary intervals) is an upper semi-continuous function, and that the definition we have given of integral is at once seen to be concomitant with that of the content of the closed set in question.

The matter becomes still plainer if we take the *internal* points of any non-overlapping set of intervals, infinite in number, and not in general abutting, and suppose a function to be defined to have the value unity at each such point, and zero elsewhere. The function so obtained is lower semi-continuous, and its integral, as we have defined it, is nothing more nor less than the sum of the series, necessarily convergent, of the lengths of these intervals.

The moment, however, that our definitions of the integrals of upper and lower semi-continuous functions have been accepted, the whole theory develops itself without a hitch. In the first place we naturally formulate the following principle, which is perfectly general, and applies equally to bounded and unbounded functions:—

(I) *A function is said to have an integral if it can be expressed as the limit (finite or infinite with determinate sign) of a monotone succession of functions, belonging to a class of functions whose integrals have already been defined, provided only that the limit of the integrals of the functions of every such succession is the same, and this limit is then called the integral of the given function.*

It is convenient to add the gloss that the integral is not regarded as existing unless it is finite.

Denoting for brevity upper and lower semi-continuous functions by the letters u and l, we are thus led to examine the nature of the functions generated as limits of monotone sequences of l-functions and u-functions. A descending sequence of u's gives us an u, an ascending sequence of l's gives us an l, but an ascending sequence of u's gives us a new function in general, which we call a lu, and a descending sequence of l's gives us a new function which we call an ul. A repetition of this process leads, on the one hand, to a re-appearance of the lu- and ul-functions, and on the other to two new types of functions, which we may call lul- and ulu-functions. It is clear that the process may be extended indefinitely, in such a manner, moreover, as to obtain functions for which a modified system of nomenclature is essential.

Confining our attention in the first instance to bounded functions, we have

to show that all bounded functions of the classes of types obtained in the manner explained possess integrals, in accordance with our principle (I). A theorem remarkable in itself, though intuitive in the light of recent theory, enables us to prove this once and for all, and at the same time gives us a different definition of integration, different in form, though equivalent in essence. The theorem follows so simply from the considerations I have exposed, that I propose to state and prove it here.

§ 2. We shall suppose that the definition of the integrals of *ul*- and *lu*-functions as the limit of the integrals of descending successions of *l*-functions, and of ascending successions of *u*-functions respectively, has been shown to be in accordance with principle (I), and that this proof has been further supplemented by a proof that, if a function is both an *ul* and a *lu*, its integral defined by both of these two distinct processes is the same. We shall also assume that term-by-term integration of monotone sequences involving functions which are *lu*- or *ul*-functions has been shown to be allowable. The proof then turns on two lemmas:—

Lemma 1.—*Given a bounded lu, we can always find an ul, nowhere less than the lu, and having the same integral, and given a bounded ul, we can always find a lu, nowhere greater than the ul, and having the same integral.*

It is evident that the one half of the statement turns into the alternative half, if we change the signs of the functions.

Let $f_1(x) \leqq f_2(x) \leqq \dots$ be a monotone ascending succession of u-functions, whose limit is the given lu-function $f(x)$.

Since $f_n(x)$ is an u-function, we may regard it as the limit of a monotone descending sequence of the elementary l-functions, and its integral as the limit of their integrals. We may, therefore, take an l-function $b_n(x) \geqq f_n(x)$, where

$$\int b_n(x)\,dx \leqq \int f_n(x)\,dx + 2^{-n-1}e.$$

If the succession $b_1(x)$, $b_2(x)$, ... is not monotone ascending, we make it so, as follows. Wherever $b_1(x) > b_2(x)$, we replace the value of $b_2(x)$ by $b_1(x)$. Let us denote the modified function by $c_2(x)$. Then $c_2(x)$ will still be $\geqq f_2(x)$, also it remains an l-function. Moreover

$$c_2(x) - f_2(x) \leqq [b_2(x) - f_2(x)] + [b_1(x) - f_1(x)],$$

whence, since both sides of this inequality represent l-functions,

$$\int [c_2(x) - f_2(x)]\,dx \leqq e(2^{-2} + 2^{-3}) < \tfrac{1}{2}e.$$

Similarly we modify b_3, b_4, ... We thus get a monotone ascending sequence of l-functions $c_2(x)$, $c_3(x)$, ..., $c_n(x)$, ... such that

$$c_n(x) \geqq f_n(x), \tag{1}$$
$$\int [c_n(x) - f_n(x)] \leqq \tfrac{1}{2}e.$$

Since the functions $c_n(x)$ and $f_n(x)$ are l-functions, this gives

$$\int f_n(x)\,dx \leqq \int c_n(x)\,dx \leqq \tfrac{1}{2}e + \int f_n(x)\,dx. \tag{2}$$

Hence, if $g_1(x)$ is the l-function which is the limit of the c_n-succession, we get, by the definition of the integral of the lu-function $f(x)$, from (2),

$$\int f(x)\,dx \leqq \int g_1(x)\,dx \leqq \tfrac{1}{2}e + \int f(x)\,dx,$$

while, from (1) $\qquad g_1(x) \geqq f(x).$

Now let us again perform the same construction, taking $\tfrac{1}{4}e$, instead of $\tfrac{1}{2}e$, and choosing each of the l-functions which we employ to be $\leqq g_1(x)$. We *thus obtain an l-function $g_2(x) \geqq f(x)$ and $\leqq g_1(x)$, and such that*

$$\int f(x)\,dx \leqq \int g_2(x)\,dx \leqq \tfrac{1}{4}e + \int f(x)\,dx.$$

Continuing thus we obtain a monotone descending sequence of l-functions,

$$g_1(x) \geqq g_2(x) \geqq \ldots \geqq g_n(x) \geqq \ldots,$$

each $\geqq f(x)$, and such that, for each value of n,

$$\int f(x)\,dx \leqq \int g_n(x)\,dx \leqq 2^{-n}e + \int f(x)\,dx.$$

If $g(x)$ be the limiting function of the g_n-sequence, then $g(x)$ is $\geqq f(x)$ and is, by definition, an ul-function, and its integral, being the limit of $\int g_n(x)\,dx$ is, as is evident from the last inequality, equal to that of $f(x)$. This proves the theorem.

Lemma 2.—*Given a bounded lul, we can always find an ul, nowhere less than the lul, and having the same integral; and given a bounded ulu, we can always find a lu, nowhere greater than the ulu, and having the same integral.*

The argument is precisely the same as the proof of Lemma 1, except that the functions $b_n(x)$ are general l-functions, instead of elementary l-functions.

§ 3. We can now at once prove the theorem which I have in mind.

Theorem.—*Given any bounded function, formed by any monotone process, such as those here described, we can find an ul-function not less than it, and a lu-function not greater than it, which have the same integral.*

Suppose, for definiteness, that the monotone succession defining the function $f(x)$ is an ascending one, say,

$$f_1(x) \leqq f_2(x) \leqq \ldots.$$

Then, without loss of generality, we may suppose that the theorem has been proved to be true for each function $f_n(x)$ of the sequence.

Let us take a lu-function, $g'_n(x) \leqq f_n(x)$, and having the same integral. Doing this for each integer n, we get a new succession, which, if not already monotone increasing, we modify as follows:—At any point where $g'_1(x) > g'_2(x)$, let us increase the value of the latter to that of the former. Denoting the modified function by $g_2(x)$, it is still a lu-function; and, since

$$g'_2(x) \leqq g_2(x) \quad f_2(x),$$

it has the same integral as before, equal to that of $f_2(x)$. We then proceed to similarly modify g'_3, and so on. Thus we have a monotone ascending sequence of *lu*-functions $g_n(x)$, whose integrals are equal to those of the functions $f_n(x)$.

The limiting function $g(x)$ of this succession is an *llu*, that is a *lu*-function, and is, of course, like every $g_n(x)$, not greater than $f(x)$. Also its integral may be obtained by term-by-term integration of the g_n-sequence; and is, accordingly, the limit of $\int f_n(x)\,dx$, that is $\int f(x)\,dx$. Thus we have found such a *lu*-function as was required.

Again, let us take an *ul*-function $h'_n(x) \geqq f_n(x)$, and having the same integral. Doing this for each integer n we get a new succession, which, if not already monotone increasing, we proceed to modify as follows:—Let $h_1(x)$ be the function whose value at each point is the lower bound of $h'_1(x)$, $h'_2(x), \ldots, h'_n(x), \ldots$ This function is easily seen to be an *ul*-function, since it is the limit of a monotone descending sequence of *ul*-functions, got by taking the lower bound of a finite number of the functions $h'_n(x)$. Similarly, let $h_2(x)$ be the function whose value at any point is the lower bound of $h'_2(x), h'_3(x), \ldots, h'_n(x), \ldots$, and so on. We thus get a monotone ascending sequence of *ul*-functions $h_n(x)$, such that

$$f_n(x) \leqq h_n(x) \leqq h'_n(x),$$

so that the integrals of these three functions are the same. The limiting function $h(x)$ is a *lul*-function, whose integral is, by definition, the limit of that of $h_n(x)$, that is of $f_n(x)$, and is therefore the same as that of $f(x)$.

§ 4. We are thus able to show immediately that all the functions of the types we have introduced possess integrals in accordance with the principles we have laid down.

This is, however, not all that the theorem just proved enables us to do. It gives us an entirely new definition of the concept of integration, which includes what we may, for convenience, call that of Darboux as a particular case. Our new definition is as follows:—

Form the integrals of all upper semi-continuous functions less than the given function, and take the upper bound of these integrals; form the integrals of all the lower semi-continuous functions greater than the given function, and take the lower bound of these integrals; then, if the upper bound of the former and the lower bound of the latter agree, the function is said to possess an integral, and the value of the integral is the common value of that upper bound and that lower bound.

The superiority of this definition over that of Darboux (or that of Riemann) consists in the fact that all bounded functions which may, in a sense easily

understood, be said to be expressible mathematically, possess an integral in accordance with the new definition.

Darboux's definition fails, in fact, because it is in general impossible to find an l-function and an u-function having the given function between them, and possessing the same integral.

The new definition succeeds because it is always possible, in all the circumstances which can arise in mathematical investigations, to find a lu-function and an ul-function between which the function to be considered lies (provided only it is bounded) having the same integral.

§ 5. When we come to consider unbounded functions no fresh difficulty arises in the application of our original principle, provided always we consider separately the modulus of the function, and the excess of the modulus over the function, or, which comes to the same thing, the two positive functions f_1 and f_2, whose difference is f and whose sum is the modulus of f. As in the other theories non-absolutely convergent integrals require separate treatment. This treatment may be the same as in the older theory, except that a limitation is removed, corresponding to the restriction implied in the Riemann definition.

In discussing unbounded functions, we may, therefore, in considering the new theory, confine our attention to positive functions, and it is clear, from what has gone before, that this is the case also with bounded functions. In other words, in the proof of all our theorems in the new theory of integration we are at liberty to suppose that the functions with which we are concerned are positive, and we need not restrict them to be bounded. In the case of an unbounded positive function, we can no longer enclose it between an ul and a lu, we can, however, always enclose it between an unbounded lul and an unbounded lu. If we include infinity ($+\infty$) as a possible value of the integral, we can then prove that all unbounded positive functions which can present themselves in mathematical reasoning necessarily possess an integral in accordance with both our definitions.

§ 6. I have now completed my sketch of the theory, regarded from the point of view of monotone sequences. If the exposition may seem somewhat long, two things are to be observed:—One is that all reference to the Theory of Sets of Points, with the various difficulties which it presents to many students, is avoided in it: and the second is that, if the development of the theory is tedious, it is not so with the applications of it. It remains to show that this is the case. For this it will be sufficient to consider two examples of different types. I take first the theorem that change of order of integration is always allowable in the case of an unbounded positive function.

As passage by monotone sequences is always permissible when we are dealing with positive quantities, it is at once evident that the theorem is true

always, if it is true for the simple bounded upper or lower semi-continuous functions with which our chain of monotone sequences began. But these functions are constant in rectangles, and their double integrals consist of the sum of the volumes of a number of rectangular parallelopipeds. Hence, in the case of these simple functions, the repeated integrals are both equal to the double integral. Hence, they must be equal in the case of any bounded, or positive unbounded function of two variables whatever.

As another example I take Schwarz's inequality, namely, that

$$\left(\int uv\,dx\right)^2 \leqq \int u^2\,dx \int v^2\,dx.$$

It is clearly sufficient to prove it for the simple functions.

Let $a_1, a_2, \ldots, a_n$ be the values assumed by one of these simple functions u, corresponding to a division of the interval of integration into n equal parts, each of length h; $b_1, b_2, \ldots, b_n$ the corresponding values of v. Then

$$\int uv\,dx = (a_1b_1 + a_2b_2 + \ldots + a_nb_n)\,h,$$

$$\int u^2\,dx = (a_1^2 + a_2^2 + \ldots + a_n^2)\,h,$$

$$\int v^2\,dx = (b_1^2 + b_2^2 + \ldots + b_n^2)\,h.$$

Thus the theorem is shown to be nothing more nor less than the assertion in the language of integrals of the well-known algebraic inequality,

$$(\Sigma a_1 b_1)^2 \leqq (\Sigma a_1^2)(\Sigma b_1^2).$$

§ 7. This is not an occasion to dwell on the usefulness of the new concept, which is sufficiently evident to anyone who has had an opportunity of consulting recent mathematical literature. It will suffice if I remind my readers that one of the reasons for its original introduction was that it enabled us to find the inverse differential coefficient of a bounded function in cases when the Riemann theory failed to help us.

That any bounded sequence may be integrated term by term follows, indeed, from the fact that it can be replaced in two ways by a pair of monotone sequences, the one pair consisting of a descending one followed by an ascending one, and the remaining pair by an ascending one followed by a descending one. We may, therefore, in the case supposed, integrate the sequence

$$[f(x+h) - f(x)]/h$$

term by term, since the incrementary ratio and the differential coefficient have the same upper and lower bounds.

Denoting then by $F(x)$, the indefinite integral of $f(x)$, and integrating between the limits x and a, we thus get

$$\underset{h\to 0}{\mathrm{Lt}}\left(\frac{F(x+h) - F(x)}{h} - \frac{F(a+h) - F(a)}{h}\right) = \int_a^x f'(x)\,dx,$$

whence, bearing in mind that $f(x)$, being continuous, is the differential coefficient of its integral, we get at once

$$f(x)-f(a)=\int_a^x f'(x)\,dx.$$

Here the sign of integration refers to integration of the generalised Lebesgue type, and it will be sufficiently evident from what precedes, that this equation is only then in general true when the sign of integration is interpreted in this sense. It may be remarked that $f'(x)$ is both a *lu* and an *ul*, and is, therefore, of a very elementary type in our scheme of functions.

On the Formation of Usually Convergent Fourier Series.

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§ 1. Series which converge except at a set of content zero, or, using the expression very commonly adopted, series which converge usually, possess many of the properties which appertain to series which converge everywhere. It becomes, therefore, of importance to devise circumstances under which we can assert the consequence that a series converges in this manner. The subject has recently received considerable attention. So far as Fourier series are concerned no result of even an approximately final character has been obtained. It may be supposed, indeed, that the results* of Jerosch and Weyl were at first so regarded,† but, if we examine them closely in the light of the Riesz-Fischer theorem, which was known previously to the results of these authors, it becomes evident that they are merely *equivalent* to the statement that the Fourier series of a function, whose square is summable, is changed into one which converges usually, if the typical coefficients a_n and b_n are divided by the sixth root of the integer n denoting their place in the series. Now it is difficult to believe that the question of the usual convergence of a Fourier series can depend on the degree of the summability of the function with which it is associated,

* 'Math. Ann.,' vols. 66 and 67.

† The result due to Fatou that a series of Fourier converges usually if na_n and nb_n converge to zero is still more special, being of course included in Jerosch's condition. For Fatou's paper, see 'Acta Mat.,' vol. 30.

and it is still more difficult to see how precisely the sixth root of n can have anything to do with it. On the other hand Weyl's method, which itself marks an advance on that of Jerosch, does not obviously lend itself to any suitable modification which would secure a greater degree of generality in the result.

The mistake is frequently made of confusing theoretical interest with practical importance in the matter of a necessary and sufficient test. Tests which are only sufficient, but not necessary, are often much more convenient. Still more frequently it is convenient to work from first principles, and not to use any test at all. Instead of employing Weyl's necessary and sufficient condition that a series should converge usually, I have attacked the problem directly. The principles I have employed do not differ essentially from those already exposed in previous communications to this Society, but the generality and interest of the results obtained in the matter in hand seem to justify a further communication.

These results are as follows:—

The Fourier series of any function whatever, of any degree of summability, and its allied series, are both of them changed into Fourier series which converge usually, if the coefficients a_n and b_n are divided by any power, however small, of the index n denoting their place in the series, in other words, they are converted into such series by the use of the convergence factor n^{-k}, $(0 < k)$, and by the use of the convergence factor $(\log n)^{-1-k}$.

More generally, they are converted into such series by the use of the convergence factor whose numerator is unity, and whose denominator is

$$l_1(n)\, l_2^2(n) \ldots l_{r-1}^2(n)\, [l_r(n)]^{2+k},\ (0 < k),\ \textit{where}\ l_r(n) = \log l_{r-1}(n),$$
$$\textit{and}\ l_0(n) = n.$$

I have thought it sufficient to prove this latter theorem for the case in which $r = 2$. With this before him the reader will easily be able, by induction or otherwise, to carry out the proof of the general result.

It will be remarked that, unlike Weyl, I have not considered general series of orthogonal functions. The theory of these functions involves usually greater analytical difficulties, but not a greater wealth of ideas, and I have thought it best, with so many problems in the theory of Fourier series still unsolved, to confine my attention to this simpler class of series. The detailed study of the theory of Fourier series seems to me to form the best possible preparation for the larger theory.

Finally, it should be noticed that the results arrived at do not in any way strengthen the probability suggested by Lusin that the Fourier series of a function whose square is summable necessarily converges usually.

Lusin's statement that this is infinitely probable seems based on the fact that in any succession of partial summations of such a series a sub-succession can be found which usually converges to the function. This is, however, quite consistent with, for example, finite oscillation except at a set of content zero. On the other hand, the results perhaps do suggest the possibility, though scarcely the infinite probability, of this latter circumstance presenting itself for all Fourier series. If this be true, every monotone succession of constants, having zero as limit, would have the effect of the special series of constants employed in the theorems of the present communication. These latter, however, are so far from being the most general successions of the monotone type that they are the Fourier coefficients both of sine and of cosine series.

§ 2. In the mode of investigation I have adopted, the following theorem and its analogue are fundamental:—

Theorem.—*Let $f(x)$ be a summable function whose typical Fourier cosine and sine constants are a_n and b_n, and let $q_1, q_2, \ldots, q_n, \ldots$, be a monotone descending sequence of constants with zero as limit, then the series*

$$\sum_{r=1} q_r (a_r \cos rx + b_r \sin rx), \tag{1}$$

oscillates boundedly at the point x, provided a succession of constants k_n can be found such that

(i) *q_n/k_n is bounded for all values of n,*

(ii) *The series $\sum_{r=1} (q_r - q_{r+1})/k_r$ converges,*

(iii) *$\int_{-\pi}^{\pi} k_n f(x+u) \sin (n+\frac{1}{2}) u \operatorname{cosec} \frac{1}{2} u \, du$ is a bounded function of n.*

Let $S_n(x)$ denote the partial summation consisting of the first n terms of (1), and let

$$s_n = \sum_{r=1}^{r=n} q_r \cos rx. \tag{2}$$

Then, since $a_r = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x) \cos rx \, dx$, and $b_r = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x) \sin rx \, dx$, we get, regarding $f(x)$ as periodic with period 2π,

$$S_n(x) = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x+u)\, s_n(u) \, du. \tag{3}$$

Now
$$2 s_n(u) \sin \tfrac{1}{2} u = \sin \tfrac{1}{2} u + \sum_{r=1}^{r=n} q_r [\sin (r+\tfrac{1}{2}) u - \sin (r-\tfrac{1}{2}) u]$$

$$= q_n \sin (n+\tfrac{1}{2}) u + \sum_{r=1}^{r=n-1} (q_r - q_{r+1}) \sin (r+\tfrac{1}{2}) u. \tag{4}$$

Therefore, by (3) and (4),

$$2\pi S_n(x) = q_n t_n + \sum_{r=1}^{r=n-1} (q_r - q_{r+1}) t_r, \tag{5}$$

where $$t_r = \int_{-\pi}^{\pi} f(x+u) \sin(r+\tfrac{1}{2}) u \operatorname{cosec} \tfrac{1}{2} u \, du,$$

and is accordingly, to a constant factor *près*, the n-th partial summation of the Fourier series of $f(x)$.

From (5) the truth of the theorem is at once evident, since by the hypothesis (iii) $t_r k_r$ is a bounded function of r, while the conditions (i) and (ii) are satisfied.

§ 3. The corresponding theorem for the allied series of $f(x)$ is as follows :—

Theorem.—*Let $f(x)$ be a summable function, whose typical Fourier cosine and sine constants are a_n and b_n, and let $q_1, q_2, \ldots, q_n, \ldots$, be a monotone descending sequence of constants with zero as limit, then the series*

$$\sum_{r=1} q_r (b_r \cos rx - a_r \sin rx) \tag{1}$$

oscillates boundedly at the point x, provided a succession of constants k_n can be found, such that

(i) *q_n/k_n is bounded for all values of n,*

(ii) *The series $\sum_{r=1} (q_r - q_{r+1})/k_r$ converges,*

(iii) *$\int_{-\pi}^{\pi} k_n f(x+u) [1-\cos(n+\frac{1}{2}) u] \operatorname{cosec} \frac{1}{2} u \, du$ is a bounded function of n.*

Let $S_n(x)$ denote the partial summation consisting of the first n terms of (1) and let

$$s_n = \sum_{r=1}^{r=n} q_r \sin rx.$$

Then, as in § 2, $$S_n(x) = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x+u) s_n(u) \, du. \tag{2}$$

Now

$$2s_n(u) \sin \tfrac{1}{2} u = \sum_{r=1}^{r=n} q_r \{\cos(r-\tfrac{1}{2}) u - \cos(r+\tfrac{1}{2}) u\}$$

$$= q_n \{1-\cos(n+\tfrac{1}{2}) u\} - q_1 (1-\cos \tfrac{1}{2} u) + \sum_{r=1}^{r=n-1} (q_r - q_{r+1}) \{1-\cos(r+\tfrac{1}{2}) u\}. \tag{3}$$

Therefore, by (2) and (3)

$$2\pi S_n(x) = q_n \tau_n - q_1 \tau_1 + \sum_{r=1}^{r=n-1} (q_r - q_{r+1}) \tau_r, \tag{4}$$

where $$\tau_r = \int_{-\pi}^{\pi} f(x+u) \{1-\cos(r+\tfrac{1}{2}) u\} \operatorname{cosec} \tfrac{1}{2} u \, du, \tag{5}$$

and is accordingly, to a constant factor *près*, the nth partial summation of the allied series of the Fourier series of $f(x)$.

From (4) the truth of the theorem is at once evident, since, by the hypothesis (iii), $\tau_r k_r$ is a bounded function of r, while q_n/k_n and $\sum_{r=1}^{r=n-1}(q_r - q_{r+1})/k_r$ are bounded functions of n.

§ 4. In applying these theorems we shall require some elementary results in the convergence of series.

Lemma 1.—*If* $$q_n = 1/[l_r(n)]^q \qquad (0<q),$$
where r has any positive integral value, including zero, and
$$l_0(n) = n,\, l_1(n) = \log n, \ldots l_r(n) = \log l_{r-1}(n),$$
then $$q_n - q_{n+1} \leq q/\prod_{s=0}^{s=r-1} l_s(n)[l_r(n)]^{1+q}.$$

Writing $$f(x) = 1/[l_r(x)]^q,$$
we have $$f'(x) = -q/\prod_{s=0}^{s=r-1} l_s(x)\,.\,[l_r(x)]^{1+q}.$$

But $$q_n - q_{n+1} = -f'(x_1) \qquad (n < x_1 < n+1),$$
$$\leq -f'(n),$$
which proves the lemma.

Cor.—*If $k<q$, and k_n has the same form as q_n, with k instead of q, the series whose general term is $(q_n - q_{n+1})/k_n$ converges.*

Lemma 2.—*If* $$q_n = 1/l_1(n)[l_2(n)]^{2+q} \qquad (0<q),$$
and $$k_n = 1/l_1(n)[l_2(n)]^{1+k} \qquad (k<q),$$
the series $\sum_{n=2}(q_n - q_{n+1})/k_n$ is convergent.

Writing $$f(x) = 1/l_1(x)[l_2(x)]^{2+q},$$
we have $$f'(x) = -f(x)\left(\frac{1}{xl_1(x)} + \frac{2+q}{xl_1(x)\,l_2(x)}\right).$$

But $$q_n - q_{n+1} = -f'(x_1) \qquad (n < x_1 < n+1),$$
whence
$$(q_n - q_{n+1})/k_n \leq -f'(n)/k_n \leq \frac{1}{l_2(n)^{1+q-k}}\left(\frac{1}{nl_1(n)} + \frac{2+q}{nl_1(n)\,l_2(n)}\right).$$

Thus the series whose convergence is under discussion is not greater than the sum of two series both known to be convergent, namely,
$$\sum_{n=2} 1/nl_1(n)[l_2(n)]^{1+q-k} \quad \text{and} \quad (2+q)\sum_{n=2} 1/nl_1(n)[l_2(n)]^{2+q-k},$$
This proves the lemma.

It should be remarked that if the index of the power of $l_2(n)$ in the

expression for q_n be $-1-q$ instead of $-2-q$, the series in question may be easily seen to be divergent.

Lemma 3.—*If*

$$q_n = 1/l_1(n)[l_2(n)]^2\,[l_3(n)]^2 \dots [l_r(n)]^{2+q},$$

and $$k_n = 1/l_1(n)\,l_2(n)\,l_3(n) \dots [l_r(n)]^{1+q},$$

the series $\Sigma\,(q_n - q_{n+1})/k_n$ *is convergent.*

Writing $$f(x) = 1/l_1(n)[l_r(n)]^{2+q} \prod_{s=2}^{s=r-1} [l_s(n)]^2,$$

we have

$$f'(x) = -f(x)\left\{\frac{1}{xl_1(x)} + \frac{2+q}{xl_1(x)l_2(x)\dots l_r(x)} + \sum_{s=2}^{s=r-1} \frac{2}{xl_1(x)\,l_2(x)\dots l_r(x)}\right\}.$$

Hence, as in preceding proof, our series is the sum of r series known to be convergent, which proves the lemma.

§ 5. In this and the next articles we shall prove certain properties as to the order of infinity of the partial summations of a Fourier series, and of its allied series, except at a set of content zero.

Theorem.—*If* $f(x)$ *be any summable function of* x, *and* $k_n = n^{-k}$, $(0<k)$, *the integrals*

$$\int_{-\pi}^{\pi} k_n f(x+u) \sin(n+\tfrac{1}{2})u \operatorname{cosec}\tfrac{1}{2}u\,du \quad and \quad \int_{-\pi}^{\pi} k_n f(x+u)[1-\cos(n+\tfrac{1}{2})u] \operatorname{cosec}\tfrac{1}{2}u\,du$$

are, for each value of x *not belonging to a certain set of zero content, bounded functions of* n.

In fact the former integral may be written

$$\int_{-\pi}^{\pi} f(x+u)(\operatorname{cosec}\tfrac{1}{2}u)^{1-k}\,[n^{-k}\sin(n+\tfrac{1}{2})\,u\,(\operatorname{cosec}\tfrac{1}{2}u)^k]\,du,$$

the absolute value of which is therefore

$$\leq \int_{-\pi}^{\pi} |f(x+u)|\,|\operatorname{cosec}\tfrac{1}{2}u|^{1-k} C_k\,du,$$

where C_k is a constant depending only on k.*

Here we have tacitly supposed that the integral just written down exists, which will certainly be the case, except for a set of values of x of zero content, in virtue of a theorem that I have proved elsewhere,† since $f(n)$ and $(\operatorname{cosec}\tfrac{1}{2}u)^{1-k}$ are summable functions of u.

In precisely the same way the second integral is proved to be less in

* See W. H. Young, "The Convergence of Certain Series Involving the Fourier Constants of a Function," 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 221.

† "Sur la généralisation du théorème de Parseval," 'Comptes Rendus,' 1912, vol. 135, p. 30; séance du 1er juillet.

absolute value than a quantity which is finite except at a set of content zero, using the boundedness of $\frac{1-\cos t}{t^k}$ instead of that of $\frac{\sin t}{t^k}$.

§ 6. We have given a separate statement and proof of the theorem of the last article because of its greater simplicity. We can, however, still further approximate to the order of infinity of the successions of our summations except at a set of content zero.

Theorem.—*If $f(x)$ be a summable function of x and*

$$k_n = (\log n)^{-1-k} \qquad (0 < k),$$

the integrals

$$\int_{-\pi}^{\pi} k_n f(x+u) \sin(n+\tfrac{1}{2})u \operatorname{cosec} \tfrac{1}{2}u \, du \quad \text{and} \quad \int_{-\pi}^{\pi} k_n f(x+u)[1-\cos(n+\tfrac{1}{2})u] \operatorname{cosec} \tfrac{1}{2}u \, du$$

are, for each value of x not belonging to a certain set of content zero, bounded functions of n.

We have

$$\begin{aligned} |\sin mu|/(\log m)^{1+k} &= |\sin mu (\log u)^{-1-k}| \{(\log mu - \log m)/\log m\}^{1+k} \\ &\leq |\log u|^{-1-k} (|\sin mu| |\log mu|^{1+k} (\log m)^{-1-k} + 1), \end{aligned}$$

and therefore $\qquad \leq C_k |\log u|^{-1-k}$,

since $\sin t |\log t|^{1+k}$ is bounded in any closed neighbourhood of the origin, and $\log mu/\log m$ remains bounded as m increases indefinitely.

Hence since

$$\operatorname{cosec} \tfrac{1}{2}u \, |\log u|^{-1-k}$$

is summable in an interval enclosing the origin not containing the point $u = 1$, the result stated with respect to the first integral is true, by reasoning similar to that employed in § 2, bearing in mind that it is clearly sufficient to prove the property in question for an interval of integration not including the point $u = 1$.

Precisely similar reasoning proves the statement with respect to the second integral, using the fact that $(1-\cos t)|\log t|^{1+k}$ is bounded.

§ 7. By a slightly more complicated process we arrive at the following result:—

Theorem.—*If $f(x)$ be a summable function of x, and*

$$k_n = (\log n)^{-1} (\log \log n)^{-1-k}, \qquad (0 < k),$$

the integrals

$$\int_{-\pi}^{\pi} k_n f(x+u) \sin(n+\tfrac{1}{2}) u \operatorname{cosec} \tfrac{1}{2} u \, du$$

and

$$\int_{-\pi}^{\pi} k_n f(x+u) [1-\cos(n+\tfrac{1}{2})] u \operatorname{cosec} \tfrac{1}{2} u \, du$$

are, for each value of x not belonging to a certain set of content zero, bounded functions of n.

We have

$$\left|\sin mu\right|\left|\log|u|\right|\left|\log|\log u|\right|^{1+k}\Big/\log m\,(\log\log m)^{1+k}$$

$$=\left|\sin mu\right|\left|\frac{\log|mu|}{\log m}-1\right|\left|\frac{\log\left|\log|mu|-\log m\right|}{\log\log m}\right|^{1+k}.$$

For convenience of printing the quantities which now occur are to be supposed all taken in absolute magnitude. Moreover, as in § 6, we may confine our attention to a conveniently small interval containing the origin, and not containing either the point unity, nor $1/e$, and we need only consider the positive part of this interval. We have then

$$\sin mu\log u\,(\log\log u)^{1+k}/\log m\,(\log\log m)^{1+k}$$

$$=\sin mu\left(\frac{\log mu}{\log m}-1\right)\left(\frac{\log(\log mu-\log m)}{\log\log m}\right)^{1+k}$$

$$\leq\sin mu\left(\frac{\log mu}{\log m}-1\right)\left(\frac{\log\log mu}{\log\log m}+1\right)^{1+k}$$

$$\leq\sin mu\left(\frac{\log mu}{\log m}-1\right)2^k\left[\left(\frac{\log\log mu}{\log\log m}\right)^{1+k}+1\right].$$

Multiplying out, we get the sum of four terms, each of which is bounded, namely

$$\frac{\sin mu\log mu\,(\log\log mu)^{1+k}}{\log m\,(\log\log m)},\qquad\frac{\sin mu\log mu}{\log m},\qquad\sin mu\left(\frac{\log\log mu}{\log\log m}\right)^{1+k},$$

and $\sin mu$,

each multiplied by 2^k.

Hence, since $\quad 1/\sin\tfrac{1}{2}u\log u\,(\log\log u)^{1+k}$

is summable, the required result follows as before, for the first integral.

In a precisely similar way it follows for the second integral.

§ 8. The general theorem that I have been establishing step by step with regard to the order of infinity of the successions of our summations is now evident. It is as follows:—

Theorem.—*If $f(x)$ is a summable function of x, the n-th partial summation of the Fourier series of $f(x)$, and the corresponding summation connected with its allied series have an order of infinity which, for every r and every k, is for every x not belonging to a certain set of content zero, less than that of*

$$l_1(n)\,l_2(n)\ldots[l_r(n)]^{1+k}.$$

The reader may be left to complete the proof by induction, or otherwise.

§ 9. We are now able to prove the main theorems which form the subject of the paper. We have only to take the fundamental theorems of §§ 2 and 3

and apply to them the suitable lemma and auxiliary theorem. These theorems enable us in the first instance only to state that the series in question oscillate boundedly except for values of x forming a set of content zero. As, however, the quantity q is at our disposal, we may perform the process of dividing by n^q in two stages, first by $n^{q'}$, and then by $n^{q-q'}$, where $0 < q' < q$. The latter process turns the finite oscillation into convergence, by Abel's Lemma. Similar remarks apply in the case of the other convergence factors.

Theorem 1.—*If $f(x)$ is a summable function, whose typical Fourier cosine and sine constants are a_n and b_n, then the series whose general terms are respectively*

$$n^{-q}(a_n \cos nx + b_n \sin nx) \qquad (0 < q)$$

and

$$n^{-q}(b_n \cos nx - a_n \sin nx)$$

both converge usually.

For, since
$$n^{-q}/n^{-k} = n^{-(q-k)} \leq 1 \qquad (k < q),$$
the condition (i) of the theorem of § 2 is satisfied.

Also by the Lemma of 1 § 4 the condition (ii) is satisfied.

Finally the condition (iii) is satisfied by § 5. Hence by the theorem of § 2 and Abel's Lemma the former series converges usually.

Similarly the latter series converges usually, using the theorem of § 3 instead of that of § 2.

Theorem 2.—*Under the same circumstances as in the preceding theorem, the series*

$$\sum_{n=2} (\log n)^{-1-q}(a_n \cos nx + b_n \sin nx) \qquad (0 < q),$$

and

$$\sum_{n=2} (\log n)^{-1-q}(b_n \cos nx - a_n \sin nx)$$

converge usually.

For since
$$(\log n)^{-1-q}/(\log n)^{-1-k} = (\log n)^{-(q-k)} \leq (\log 2)^{-(q-k)} \qquad (k < q),$$
the condition (i) of §§ 2 and 3 is satisfied.

The condition (ii) is satisfied in virtue of the Lemma 1 of § 4.

Finally the condition (iii) is satisfied by § 6.

Hence by §§ 2 and 3 and Abel's Lemma the theorem is true.

Theorem 3.—*Under the same circumstances, the series*

$$\sum_{n=3} (\log n)^{-1}(\log\log n)^{-2-q}(a_n \cos nx + b_n \sin nx),$$

$$\sum_{n=3} (\log n)^{-1}(\log\log n)^{-2-q}(b_n \cos nx - a_n \sin nx),$$

converge usually.

Here we take $$q_n = 1/l_1(n)\,[l_2(n)]^{2+q},$$
and $$k_n = 1/l_1(n)\,[l_2(n)]^{1+k}, \qquad (k < q).$$
We then have $$q_n/k_n = 1/[l_2(n)]^{1+q-k},$$
showing that the condition (i) of §§ 2 and 3 is satisfied.

The condition (ii) is satisfied in virtue of the Lemma 2 of § 4.

Finally the condition (iii) is satisfied by § 7.

Hence by §§ 2 and 3 the theorem is true, using once more Abel's Lemma.

Theorem 4.—*Under the same circumstances the series*

$$\Sigma\, q_n(a_n \cos nx + b_n \sin nx) \quad \textit{and} \quad \Sigma\, q_n(b_n \cos nx - a_n \sin nx),$$

where $$q_n = 1/l_1(n)\,[l_2(n)]^2 \ldots [l_r(n)]^{2+q} \qquad (0 < q),$$

converge usually.

Here we take
$$k_n = 1/l_1(n)\,l_2(n) \ldots [l_r(n)]^{1+k} \qquad (k < q).$$

We then have
$$q_n/k_n = 1/l_2(n)\,l_3(n) \ldots [l_r(n)]^{1+q-k},$$
showing that the condition (i) of §§ 2 and 3 is satisfied.

The condition (ii) is satisfied in virtue of Lemma 3 of § 4.

Finally the condition (iii) is satisfied by § 8.

Hence by §§ 2 and 3 the theorem is true, using once more Abel's Lemma.

§ 10.* If, instead of the theorem that $\int f(x+t)\,g(t)\,dt$ exists as a function of x *almost* everywhere, when f and g are summable functions, we employ the connected result that this function exists *everywhere* and is continuous, when the summabilities of f and g are suitably connected, we obtain in a similar manner information as to the order of infinity *everywhere* of the partial summations of the Fourier series of the various types of functions. In this way not only are results such as those exposed in my papers "On the Convergence of Certain Series, etc.,"† and "On the Fourier Series of Bounded Functions,"‡ confirmed, but further new ones are obtained.

§ 11. On the other hand, Mr. G. H. Hardy points out that it is possible to slightly extend the results of this paper as regards Fourier series by utilising a theorem of Lebesgue's instead of the above-mentioned theorem. Indeed, we are thus enabled, in the case both of the Fourier series and its allied series, to replace the two's by unities in the general convergence factor. Moreover, in the case of the Fourier series—as distinct, be it said, from the allied series—we can, as he remarks, go still farther and obtain a further slight, but, as it

* §§ 10–12 have been added during the passage through press, Feb. 8, 1913.

† *Loc. cit. supra.*

‡ 'Lond. Math. Soc. Proc.,' 1912, Ser. 2, vol. 12.

appears to me, important extension, by utilising an additional artifice already employed by Messrs. Hardy and Littlewood.

§ 12. We may similarly, when desirable, instead of the connected result referred to in § 10, use a property of an integral of a function of given kind of summability, such as follows from considerations exposed in my paper on "Summable Functions and their Fourier Series."*

On a Cassegrain Reflector with Corrected Field.

By R. A. Sampson, F.R.S.

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(Abstract.)

The purpose of this memoir is to discover an optical appliance which shall correct in a practical manner the faults in the field of a Cassegrain reflector, while leaving unimpaired its achromatism and the characteristic features of its design, which gives a focal length much greater than the length of the instrument, combined with a convenient position of the observer. The question touches an investigation by Schwarzschild† as to what can be done with two curved mirrors the figures of which are not necessarily spherical. With these he corrects spherical aberration and coma, but in order to secure a flat field he is led to a construction in which the second mirror, which is between the great mirror and its principal focus, is concave, and therefore shortens the effective focal length, in place of increasing it. The deformations from spherical figures are also so great, especially for the great mirror, as to leave it doubtful whether the construction discussed could ever be the model for practicable instruments. If we keep to the Cassegrain form, spherical aberration and coma may equally be corrected by deformations of the mirrors which, though large, are less extreme, but there remains a pronounced curvature of the field. For this reason I am led, in the present memoir, to consider more complicated systems produced by the interposition of systems of lenses. Achromatism can be preserved completely for a single focus if there are three lenses of focal length determined when their position are given, and if all are made of the same glass. One of these lenses, which I

* 'Roy. Soc. Proc.,' 1912.

† 'K. Gesell. d. Wissenschaften zu Göttingen, Math.-Phys.-Classe,' Neue Folge, 1905, vol. 4.

call the reverser, is silvered at the back and replaces the convex mirror; the other two are placed close together in the way of the outcoming beam, about one-third of the distance from the great mirror to the reverser; the members of this pair, which I call the corrector, are of nearly equal but opposite focal lengths, introducing very little deviation in the ray but an arbitrary amount of aberration, according to the distribution of curvatures between the two faces of each lens. All the surfaces are supposed spherical except that of the great mirror. The essential problem is to bring the necessary work into a form that will allow unknown quantities which express the distribution of curvature between the faces of each lens to be carried forward algebraically. The methods employed are those of a recent memoir by the author,* and a part of the paper is occupied in working out expressions to which this theory leads, for thin lenses, systems of thin lenses, mirrors, reversers and the like, and it may be regarded as an expansion and working illustration of that memoir. This part does not lend itself to summary. When the expressions are obtained the solution proceeds in a straightforward manner, by approximation, which is somewhat complicated owing to the number of considerations which it is necessary to keep in view, but is not otherwise difficult. The solution is completed at the stage where the unextinguished aberrations are considered negligible.

Before determining the aberrations the system was made achromatic in respect to the normal, that is to say, the linear or ideal scheme, both in respect to position and magnification of the image. Hence, at the end of the above steps, there might remain chromatic differences of the various aberrations, and it is a necessary condition that these also should prove inconsiderable. When the curves of the lenses were given by a final solution the aberrations were calculated, to the third order without approximations, for the whole system for two different refractive indices, viz., $\mu = 1{\cdot}5200$ and $\mu = 1{\cdot}535200$.

The object aimed at was to extinguish spherical aberration, coma, and curvature of the field, and to keep astigmatism down to very narrow limits. The field whose curvature is contemplated is the field which passes through the circular images that lie midway between the two focal lines in a system which is free from coma. Hence, in the system sought, the images of all points at the focal plane would be strictly circles, which increased in diameter with the square of the angular breadth of the field.

Distortion comes into the system with the separated lenses, but this does not impair the images of points, and so long as it does not reach an

* "A New Treatment of Optical Aberrations," 'Phil. Trans.,' vol. 212, pp. 149–185.

unmanageable amount it may be dealt with as a correction, calculated and applied to any measures that are made.

In the following particulars of the construction, together with its outstanding defects, the notation, though not exactly in the standard form, almost explains itself; thus all the quantities with suffix 2, for example, relate to the reverser, a_2 being its semi-aperture, t_2 its thickness, R_2, R_2' the radii of its anterior and posterior surfaces. Similarly, the suffixes 4, 6, relate to the first and second lenses of the corrector, while the quantities d are the distances from surface to surface. The unit employed is 1 inch. The quantity ϵ gives the departure of the great mirror from a parabolic figure, on such a scale that $\epsilon_0 = 1$ would give a sphere. Hence the figure is five-sixths of the way from a sphere to a paraboloid. The greatest angle between the ray and the normal to any surface is 11°, at emergence from the second surface of the first lens of the corrector.

For comparison the particulars of a Newtonian of equal focal length and aperture and paraboloidal mirror are also given.

It may be remarked that if the solution had been made originally for the greater refractive index in place of the smaller, the residual aberrations shown by the other would apparently have been less in place of greater, so that those for which the solution was made are to be regarded as the significant ones.

Great mirror—		
Aperture	$2a_0 = 40{\cdot}0$	
Radius of curvature	$R_0 = -400{\cdot}000$	
Figure	$\epsilon_0 = +0{\cdot}16468$	
		$d_1 = +132{\cdot}013$
Reverser—		
Aperture	$2a_2 = 16{\cdot}2$	
First surface	$R_2 = +211{\cdot}603$	
Silvered surface	$R_2' = +221{\cdot}289$	
Thickness	$t_2 = 2{\cdot}000$	
		$d_3 = +90{\cdot}676$
Corrector, first lens—		
Aperture	$2a_4 = 12{\cdot}2$	
First surface	$R_4 = -144{\cdot}298$	
Second surface	$R_4' = +48{\cdot}824$	
Thickness	$t_4 = 1{\cdot}250$	
		$d_5 = +0{\cdot}500$
Ditto, second lens—		
Aperture	$2a_6 = 12{\cdot}2$	
First surface	$R_6 = -4138{\cdot}559$	
Second surface	$R_6' = -38{\cdot}285$	
Thickness	$t_6 = 1{\cdot}500$	
Distance to principal focus	$d_7 = +71{\cdot}377$	
Focal length	$f_7' = +508{\cdot}802$	
Distance of principal focus beyond surface of great mirror	$+\ 33{\cdot}290$	
Whole length of instrument	$167{\cdot}3$	

Specification of Field at Angular Radius $34{\cdot}4' = \tan^{-1} 0{\cdot}01$.

	$\mu = 1{\cdot}5200$.	$\mu = 1{\cdot}5352$.	[Newtonian.]
Radius of least circle of aberration	$0{\cdot}000''$	$-0{\cdot}007''$	$0{\cdot}00''$
„ comatic circle	$-0{\cdot}005$	$+0{\cdot}069$	$+0{\cdot}80$
„ focal circle	$+0{\cdot}370$	$+0{\cdot}566$	$-0{\cdot}41$
Distortional displacement	$+6{\cdot}75''$	$+7{\cdot}18''$	$0{\cdot}00$
Curvature of field	$-1/16282$	$-1/542{\cdot}3$	$-1/508{\cdot}8$

On a New Analytical Expression for the Representation of the Components of the Diurnal Variation of Terrestrial Magnetism.

By GEORGE W. WALKER, M.A., A.R.C.Sc.

(Communicated by Prof. J. H. Poynting, F.R.S. Received January 8,— Read January 30, 1913.)

In any enquiry as to the cause or causes that contribute to daily or seasonal change of a periodic character in any observational quantity, the primary step is the determination of a simple and comprehensive expression for the dominant features of the phenomenon.

The periodic character of the variations of an element of terrestrial magnetic effect, such as declination, horizontal force, or the equivalent geographical components of force, is evident on almost every daily record obtained. When the hourly values are set out and properly cleared from non-periodic change (a problem of considerable subtlety), the historic method is to compute the Fourier harmonic components. Another method that appears to possess great power is that so successfully carried out by Dr. W. N. Shaw in representing the daily and seasonal changes of meteorological elements by means of "isopleths."

If a Fourier analysis reveals the existence of a limited number of dominant terms, that is so far satisfactory and provides definite material on which the theorist may work. But, in the case of the terrestrial magnetic elements, there is abundant evidence to show that even four Fourier terms give a very inadequate representation of the facts, and, with the exception of Dr. Schuster's valuable memoirs based on consideration of the first two terms in the diurnal variation, the subject is in rather a dismal state.

The problem has attracted my attention for several years, and the following

ideas to which I have been led appear to me to provide another method of attack which may be of value.

Since the Fourier representation of the magnetic diurnal variation does not converge rapidly, one naturally doubts whether the 12-hour, 8-hour, 6-hour, etc., terms really correspond to a definite physical cause, and the next step is the question whether the phenomena are not simply diurnal and nothing else.

One recalls the simple pendulum. Anyone who attempted to represent the motion, as an observed thing, by means of circular functions would not be very likely to arrive at the simple gravitational law, but the introduction of the appropriate elliptic function having one definite real period clears up the matter. Another forcible illustration, suggested to me by Dr. Poynting, is that while one takes food at more or less definite hours, yet a Fourier representation is quite unsuitable and the phenomena are purely diurnal.

Looking at magnetic traces day by day, one is impressed very strongly with the idea of a magnetic field fixed with regard to the sun, within which the earth rotates. This is true, not only with regard to the regular daily variation, but also with regard to irregular disturbances that occur so frequently between 20 h. and 24 h., a bay in the curve occurring one evening is often reproduced with startling similarity about 24 hours after, generally less than 24 hours rather than more.

Guided by this notion, I endeavoured, in a purely tentative way, to obtain simple functions that would imitate the general features of the average daily curve for a magnetic element, the essential point being that the function should recur in 24 hours, but not in any sub-multiple of 24 hours.

The function

$$y \propto \sin t/(1+k\cos t)$$

at once occurred as going a good way towards a rough representation.

The Curve I on the diagram (fig. 1) is actually $y = -2\sin t/(1+0{\cdot}7\cos t)$. We note that $\int_0^{2\pi} y\,dt = 0$ as is required.

To plot the corresponding curve

$$y \propto \cos t/(1+k\cos t)$$

was an obvious step.

In order now to make $\int_0^{2\pi} y\,dt = 0$ we require to shift the origin of y, and so Curve II represents

$$y = \left\{1-\frac{1}{(1-k^2)^{\frac{1}{2}}}-\frac{k\cos t}{1+k\cos t}\right\} = \left\{\frac{1}{1+k\cos t}-\frac{1}{(1-k^2)^{\frac{1}{2}}}\right\},$$

for $$k = 0{\cdot}7.$$

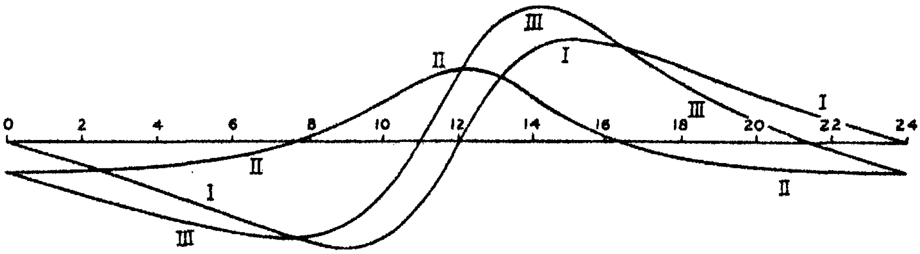


FIG. 1.—Graphs of the functions.

The curve III is obtained by the simple addition of I and II. We have only to look at the curves* to see that III represents the characteristic features of the declination or west component for either Kew, Potsdam, or Paris.

The essential feature of a declination curve is that the morning minimum is less in magnitude than the afternoon maximum, and that the curve is flatter at the minimum than it is at the maximum.

The turning points can be shifted by changing k and the relative proportions of I and II. A great variety of curves can be obtained in this way, and I am satisfied that any component, west, north, or vertical, can be imitated in essential features.

The general form suggested is thus

$$y = -k\frac{(k_1 \sin t + k_2 \cos t)}{(1+k\cos t)} + k_3\left\{1 - \frac{1}{(1-k^2)^{\frac{1}{2}}}\right\},$$

wherein k, k_1 and k_2 are at our disposal and the origin of t is also arbitrary.

It seems to me rather remarkable that curves essentially unsymmetrical can be imitated in this way. Doubtless there are many other expressions of a similar type which could be used and the above is probably only the principal part of the correct formula.

It is not at once clear how a term $(1+k\cos t)$ in the denominator can arise physically, but the following tentative suggestion is worth considering.

There are some reasons for supposing that the magnetic field of the earth is in some way connected with the intensity of solar radiation in the upper regions of the atmosphere. Now the intensity of radiation is approximately represented by a term of the form $I_0 e^{-\mu \sec z}$, where z is the zenith distance of the sun, and as $\cos z = \sin\lambda \sin\delta + \cos\lambda\cos\delta\cos h$, where λ is the latitude, δ the sun's declination, and h the hour angle, the occurrence of the term $(1+k\cos t)$ is suggested, but, of course, careful examination of local and seasonal effect is required before it can be accepted.

The curves of diurnal variation of the magnetic elements always indicate

* Arrhenius, 'Cosmical Physics,' or Chree, 'Phil. Trans.,' 1903, A, vol. 202.

subsidiary fluctuations about the beginning and end of the day. These arise in the main from the inclusion in the tabulated mean hourly values of those large irregular disturbances that occur, as has been pointed out, late in the day. It would seem to be worth while to examine whether, having represented the chief features by a term of the type given, we could represent the small unexplained balance by another term of the same type but with different constants.

Any typical curve of diurnal variation of a magnetic element cuts the axis twice in 24 hours, and has a principal maximum and a principal minimum.

We may now indicate how the constants in the formula would be chosen so as to get the closest representation of the experimental curve. The general scale of the curve fixes the most important relation of all between the constants. It would be most natural to take the extreme range as fairly accurately known.

Again, the times of occurrence of zeros are given by

$$\tan(t-t_0)/2 = \frac{kk_1 \pm \{k^2k_1^2 + 2k_2^2[1/(1-k^2)^{\frac{1}{2}} - 1]\}^{\frac{1}{2}}}{k_2\{1-[(1-k)/(1+k)]^{\frac{1}{2}}\}},$$

and those of the maximum and minimum by

$$\tan(t-t_0)/2 = -\frac{k_2 \pm \{k_2^2 + k_1^2(1-k^2)\}^{\frac{1}{2}}}{k_1(1-k)}.$$

We shall not be able in general to satisfy all these relations, for when the scale is prescribed only three more conditions can be satisfied. In any particular case we should have to decide what points are most accurately given by the curve. For instance, with declination in these latitudes there would be little hesitation in taking the maximum and the minimum with the zero occurring about noon as much more accurately determined than the zero towards midnight, and so we should take these three to determine the constants and let the remaining zero take care of itself. The divergence will in fact be a measure of the correctness of the representation.

I had intended to reserve these considerations for inclusion in an extended examination of magnetic diurnal variation which I have in progress; but as this method of considering functions that recur only once in 24 hours, and are capable of representing unsymmetrical curves, is of considerable interest, and I believe novelty, this brief account is offered now.

A Spectro-photometric Comparison of the Emissivity of Solid and Liquid Copper and of Liquid Silver at High Temperatures with that of a Full Radiator.

By C. M. Stubbs, M.A., M.Sc.

(Communicated by Prof. F. G. Donnan, F.R.S. Received January 9,—Read January 30, 1913.)

(From the Muspratt Laboratory, University of Liverpool.)

Introductory.

In a paper which appeared recently in these 'Proceedings'* Dr. Prideaux and the author communicated the results of a spectro-photometric comparison of the emissivity of solid and liquid gold at high temperatures with that of a full radiator, or "black body." For solid gold, the curve for relative emissivity against wave-length was shown to be similar to, but not identical with, that for absorptivity at low temperatures determined by other workers; whether the difference was due to a difference in the structure of the surfaces examined, or to a real temperature coefficient of the absorptivity, remained an open question. At the high temperatures employed no appreciable temperature coefficient of the relative emissivity could be discovered, for either the solid or liquid metal. At the melting-point, however, there is an abrupt change in emissivity, the curve for the liquid differing considerably from that for the solid.

In the present paper is described a similar investigation of the emissivity of copper and silver.

Apparatus and Method.

The general method pursued and the apparatus used were the same as described in the former paper, with the exception of such changes and modifications as will now be referred to.

The "black body" used in the present research was of the Lummer-Kurlbaum type.† It had certain peculiarities which perhaps are worthy of description. Instead of the usual porcelain tube, an iron tube 58 cm. long, 5 cm. in internal diameter, and with walls 3 mm. thick was used; the radiating surface consisted of a well-fitting iron block, 2 cm. in thickness; the radiating chamber was 4·7 cm. in length, the nearest diaphragm to the radiating surface being of iron, 4 mm. thick, and with an aperture 1·6 cm. in diameter.

* 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 451.

† 'Ann. d. Phys.,' 1901, vol. 5, p. 829.

In front of the radiating chamber were four other diaphragms, made of sheet nickel, which withstands oxidation well. The temperature was measured by a thermocouple, enclosed in a thin-walled tube, which passed through the diaphragms immediately below the apertures, and fitted into a hole bored in the radiating block; on the reverse side, a second checking thermocouple passed through suitable diaphragms and fitted into a hole bored in the centre of the radiating block. The various diaphragms and radiating block were kept in their relative positions by stout iron rods, but could be moved collectively along the iron tube; the radiating chamber could thus by actual trial be made to coincide with the region of uniform temperature. The heating was by means of two windings of "nichrome" No. 22 resistance wire, on independent circuits, insulated from each other and from the iron tube by several layers of asbestos paper; the outer one was, as suggested by Waidner and Burgess,* wound more closely at the ends than in the middle. To sum up the advantages obtained, these were (1) evenness of temperature distribution through the nature of the winding, the conductivity of the walls of the radiating chamber, and the freedom of movement of the latter relative to the tube, and (2) automatic lining of the walls of the chamber, on heating, with iron oxide, which possesses a good degree of "blackness." The fact that at high temperatures a narrow hole bored in the centre of the radiating surface was invisible showed that very approximately full radiation was obtained. The whole "black body" might probably with advantage have been made on a somewhat smaller scale.

Both copper and silver had to be kept in a reducing atmosphere, in order to avoid surface oxidation of the former, and the dissolution of oxygen in the latter, resulting in a considerable lowering of freezing-point and consequent uncertainty in temperature-measurement, and possibly also in a change in emissivity.

In the case of copper, the metal was contained in a silica pot inside a vertical iron tube 40 cm. long and 5 cm. in internal diameter, and closed at the bottom. This tube possessed a hollow water-cooled cap which could be screwed tightly on. Through the centre of the water-chamber was soldered a tube sufficiently wide to allow spectro-photometric observation of the copper; other smaller tubes passing through the water-chamber were for the thermocouple, and for ingress and egress of hydrogen. Over the central aperture was laid a thin microscope cover-glass, vaselined down at the edges, through which observations were taken. A suitable tap allowed the observation-tube to be closed from the air when the cover-glass was removed for cleaning. This arrangement proved quite satisfactory, and a slow stream of hydrogen passing

* 'Bull. Bur. Standards,' 1907, vol. 3, p. 165.

through the tube and out without burning kept the copper from oxidation. The width of the iron tube was such that the reflection of its walls was not visible in the copper mirror. The image of the under surface of the water-cooled cap, illuminated by the light of the furnace, would, however, be visible. This surface was, therefore, lampblacked; though as a matter of fact a simple calculation showed that the glowing parts of the heated tube were so far from the top that no appreciable influence would be exercised on the apparent emissivity of the copper, even if the bottom of the water-cooler were far removed from blackness. In order to balance the loss of heat by conduction to the water-cooled end, the wall of the upper half of the iron tube was turned thin, and the whole tube then wound with "nichrome" resistance wire over asbestos paper, and placed within a large vertical platinum-wound resistance furnace whose heating-tube was 22 cm. long and 12 cm. in diameter. With the aid of the heat generated by the passage of an auxiliary current through the winding on the tube, the desired temperatures were easily obtained.

In the case of silver, where access of oxygen below a red heat has not to be avoided, the metal was heated in a furnace whose heating-tube was a silica one wound with "nichrome" wire. On to this tube fitted closely the water-cooled cap described above. Any appreciable access of air was thus avoided, and a reducing atmosphere was kept by placing a quantity of powdered graphite beneath the crucible containing the silver. The metal was observed, as in the case of copper, through a thin cover-glass. As was necessary for comparative purposes, the "black body" also was viewed through this glass. The latter was in all cases cleaned from time to time.

The same care as described in the former paper was taken to calibrate and check the thermocouples, and the spectro-photometer with its comparison lamp. Any change in the latter was checked and allowed for by making observations of "black body" radiation several times during the course of the experiments. In measuring the temperature of the metals only one thermocouple was used, which was inserted about 1·5 cm. into the metal. Owing to the sharp temperature-gradient above the surface the temperatures indicated were a little too low, but were corrected, as described in the former paper on gold (p. 456), by observing the indication at the melting-point.* The corrections necessary were small, usually about 3°.

* In the case of copper, allowance was made for the depression of freezing-point caused by dissolved hydrogen. The latter amounts to 0·54 mgrm. per 100 grm. of metal, according to Sieverts and Krumbhaar ('Zeits. phys. Chem.,' 1910, vol. 74, p. 292). From the depression constant given for copper by Heyn ('Zeits. anorg. Chem.,' 1904, vol. 39, p. 20), this would involve a depression of freezing point of less than 0·5°.

A method was devised of compensating automatically for the troublesome variable thermal E.M.F. of the potentiometer, mentioned in the former paper (p. 457), which, as such thermal E.M.F.'s occur frequently in these instruments, may be worth a brief description. A_1A_2 and B_1B_2 (fig. 1) are two of the pairs of circuit terminals on the potentiometer. The thermal E.M.F. of the instrument tends to create a small difference of potential between A_1 and A_2, or between B_1 and B_2, whichever pair may be put into the potentiometer circuit by the circuit switch. E_1 is a battery which runs down through the high resistance R and the low slide-resistance XY. With the circuit switch on A_1A_2, and the main potentiometer current temporarily disconnected, the slider Z is adjusted so that the fall in potential along ZY is equal to that between A_1 and A_2, due to the thermal E.M.F.; the galvanometer will accordingly give no deflection. If now E_2 be the source of the E.M.F. to be measured, and connections be made as in the diagram

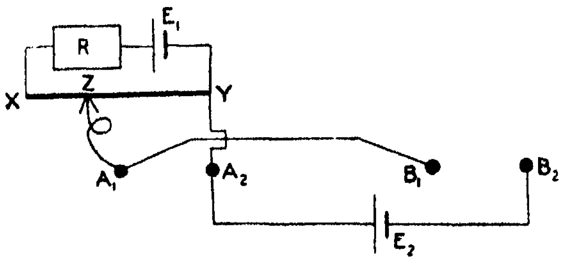


FIG. 1.—Diagram of method of compensating for thermal E.M.F.

it is clear that between B_1 and B_2 there will be a fall in potential equal to E_2, together with the fall along ZY; this latter will exactly balance the thermal E.M.F., and consequently the reading of the instrument will correspond with the true E.M.F. E_2.

Results and Conclusions.

(1) *Copper.*—About 400 grm. of pure electrolytic copper were used, the internal diameter of the containing pot being 4·2 cm. and the depth of metal about 3·5 cm. The solid copper surfaces whose emissivity was measured were prepared as follows:—The block of previously fused electrolytic copper was turned flat in the lathe, then treated successively with four grades of emery paper, and finally polished on chamois leather with a little "Globe" metal polish, the surface being washed with benzene after polishing. The use of rouge was avoided, as it is liable to tarnish soft metals, and actually did so in the previously investigated case of gold. Brilliant mirrors were obtained which, on heating, showed practically no trace of filming due to impurity.

Even the best mirror was, however, marked with a few fine scratches. Tate, also,* has recently found it impossible to get a perfect copper mirror by polishing. The area occupied by these scratches would, however, be so small as scarcely to affect the emissivity; and, in fact, they were invisible when the metal was heated to glowing. The surface showed no apparent deterioration until within about 10° of the melting-point, when re-crystallisation rapidly set in, involving reflection of light from the furnace walls by the roughened surface.

A perfect mirror surface of liquid copper, free from film, was obtained without difficulty.

In Table I are given the values obtained for the relative emissivity of solid and liquid copper, calculated as shown in the former paper (p. 458). The capitals at the head of the columns indicate, in alphabetical order, the order of the experiments. The approximate temperatures are also given. In this and subsequent tables emissivities and absorptivities are stated in percentage numbers.

Table I.—Relative Emissivity of Copper.

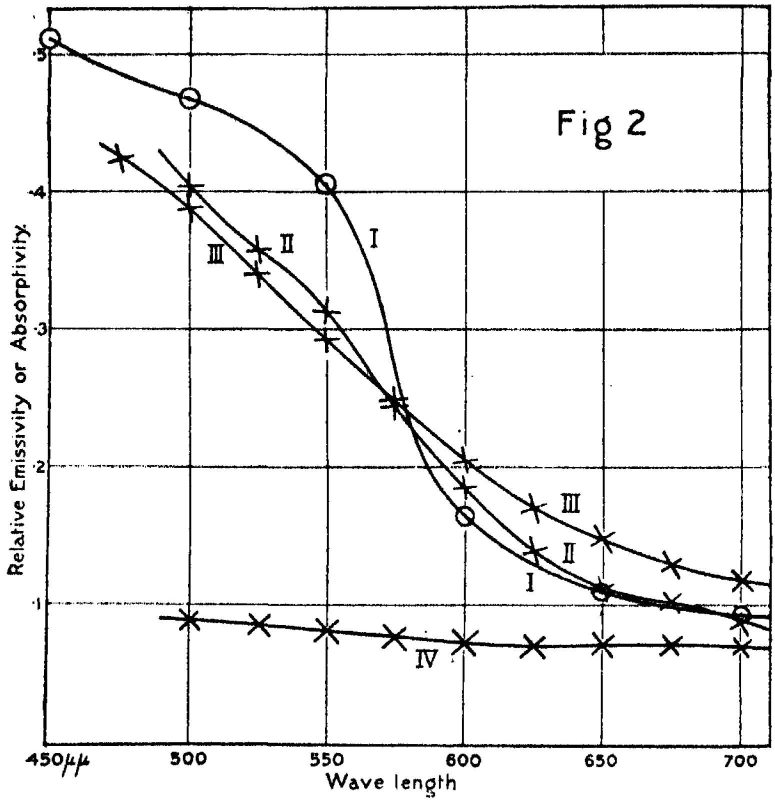
Wave-length in $\mu\mu$.	Solid.				Liquid.			
	D. 989°.	C. 991°.	D. 1053°.	Mean.	B. 1090°.	A. 1127°.	C. 1174°.	Mean.
700	10·1	7·7	9·4	8·7	10·6	13·0	12·4	11·8
675	10·7	9·5	11·1	10·2	12·3	13·9	13·0	12·9
650	11·6	10·4	12·4	11·2	14·8	15·2	14·6	14·8
625	14·7	13·0	15·0	13·9	17·1	17·8	16·7	17·1
600	19·3	17·3	20·1	18·5	21·0	21·0	19·7	20·5
575	24·6	23·7	25·7	24·4	25·1	25·0	24·4	24·8
550	31·7	30·8	31·9	31·3	29·8	29·5	28·6	29·3
525	35·2	35·5	36·7	35·7	33·0	34·0	34·9	34·0
500	41·5	38·9	42·1	40·4	37·4	38·1	40·2	38·7
475	—	—	—	—	37·4	47·3	—	42·4

The solid copper mirror used for experiment D was not so perfect as that used for C, and one or two small red spots due to markings on the surface were visible amid the otherwise greenish light from the copper. In calculating the mean, therefore, only half weight is given to the numbers in the first and third columns. It is probable that even so the "mean" values err on the high side. In calculating the mean values for the liquid only half weight is assigned to experiment A, there being reason to suspect the corresponding "black body" readings of less accuracy than usual. The

* 'Phys. Rev.,' 1912, vol. 34, p. 321.

mean values of the relative emissivity at the various wave-lengths are shown graphically by the Curves II and III in the diagram (fig. 2).

It is evident that, as in the case of gold, the emissivity of copper is discontinuous at the melting-point, the difference, however, between that of the solid and of the liquid being less marked. No previous quantitative



I. Absorptivity, solid copper; II. Relative emissivity, solid copper; III. Relative emissivity, liquid copper; IV. Relative emissivity, liquid silver.

measurements have been made of the radiation from solid copper; but some on liquid copper have been made by Burgess.* The following table embodies his results:—

Wave-length in $\mu\mu$.	Relative emissivity of liquid copper at			
	1075°.	1125°.	1175°.	1225°.
650 550	17 47	15 38	14 32	13 28

* 'Bull. Bur. Standards,' 1909, vol. 6, p. 111.

The wide disparity between his values and the author's is apparent; nor in the author's results is there any evidence of such a decrease of relative emissivity with rise in temperature as Burgess shows. His results are undoubtedly in error, due largely to lack of monochromatism of the coloured glasses used in his pyrometer (which in a case such as the present, where emissivity varies rapidly with wave-length, might introduce considerable errors), and probably also to the far less favourable experimental conditions of his work.

The reflectivity of copper at ordinary temperatures has been measured by several, the surface being prepared by polishing in the work of Hagen and Rubens,* Minor,† and Tool.‡ The first named determined the reflectivity directly, the other two by calculation from other optical constants. The following values for the absorptivity (1−R, where R = reflectivity) are given by their results:—

Wave-length in $\mu\mu$.	Hagen and Rubens.	Minor.	Tool.	Wave-length in $\mu\mu$.	Hagen and Rubens.	Minor.	Tool.
700	9·3	—	—	575	—	29·8	—
660	—	—	15·4	560	—	—	39·9
650	11·0	—	—	550	40·5	41·6	—
640	—	—	15·9	540	—	—	42·4
630	—	19·5	—	535	—	43·8	—
620	—	—	17·2	520	—	—	44·0
600	16·5	—	18·6	500	46·7	44·5	44·9
589·3	—	25·9	—	480	—	—	46·1
580	—	—	23·3	450	51·2	49·5	—

The values of the different workers do not agree very well, the differences being no doubt largely due to variation in the conditions of preparation of the surface. All agree, however, in deviating strikingly from the values for the relative emissivity of the solid metal given in Table I. Hagen and Rubens' values are shown graphically by the curve I in the diagram. The deviation is in all cases greatest for the shorter wave-lengths. Thus for wave-length 550 $\mu\mu$ (green) all three workers agree in placing the absorptivity at about 41 per cent.; the author's value for relative emissivity is 31 per cent. Again, in the region 560 to 590 $\mu\mu$, the author's curve does not show the remarkable flexure which is characteristic of the others', though there are signs of a slight bend.

As may be shown by a simple calculation, the discrepancy cannot be due to the temperature of the surface being lower than indicated by the thermo-

* 'Ann. d. Phys.,' 1902, vol. 8, p. 17.

† 'Ann. d. Phys.,' 1903, vol. 10, p. 609.

‡ 'Phys. Rev.,' 1910, vol. 31, p. 14.

couple. For at (say) 1000° C. the total energy radiated by a "black body" is, by Stefan's law, $5{\cdot}3 \times 10^{-5} \times 1273^4$ ergs per square centimetre per second. The thermal conductivity of copper at ordinary temperatures is such that, with a temperature-gradient of 1° per centimetre, 0·91 grm. calories, or $4{\cdot}2 \times 10^7 \times 0{\cdot}91$ ergs, pass per square centimetre per second. Thus, if X be the temperature-gradient in degrees per centimetre which a "black body" at 1000° and with the conductivity of copper would need for radiated energy to be continually replaced,

$$5{\cdot}3 \times 10^{-5} \times 1273^4 = X \times 4{\cdot}2 \times 10^7 \times 0{\cdot}91,$$

whence $X = 3{\cdot}7$. Since now most of the energy radiated by a "black body" at 1000° C. is in the infra-red, where the reflectivity of copper is very high, and emissivity therefore very low, it is safe to say that copper would radiate less than 1/10 as much as a "black body"; and the temperature-gradient necessary is reduced to less than 0·37° per centimetre. Or, making every allowance for change in conductivity with temperature, etc., a temperature-gradient of less than 1° per centimetre would be required, whereas an error of 17° would be needed to explain the difference given above between the values at wave-length 550 $\mu\mu$.

Again, loss of polish on heating would result in reflection from the furnace walls, and therefore a greater instead of a less value for the relative emissivity. The conclusion is unavoidable that the absorptivity in the visible spectrum of a polished copper surface changes on heating. Such a change in the case of gold was suggested, though left open to question, by the results given in the former paper (p. 461). It is significant that the relative emissivity curve for solid copper tends to approach the absorptivity curve at long and short wave-lengths, but to make the intermediate flexure which is characteristic of all copper surfaces, even unpolished ones,* much less marked. This tendency is carried out to a much greater degree in the curve for liquid copper, which is without flexure, but still approaches the absorptivity curve at extreme wave-lengths. Similar remarks apply in the case of gold. It seems at least plausible that, however invariable optical constants may be with temperature in the case of such metals as platinum,† the atomic or molecular peculiarities which cause the rapid variation, in the visible spectrum, of the optical constants of copper and gold are diminished as the temperature rises and the kinetic energy of the atoms increases, a further diminution appearing suddenly when inter-molecular constraint is further relieved at the melting-point.

An investigation which the author has not the facilities for carrying out,

* For an example of these, the recent work of Tate ('Phys. Rev.,' 1912, vol. 34, p. 321) may be referred to.

† Rubens, 'Phys. Zeits.,' 1910, vol. 11, p. 139.

but which may be suggested as a way of definitely settling the behaviour of copper, would be, after determining the emissivity of a heated solid copper surface, to let it cool down, and directly determine its reflectivity, or better still, to determine the reflectivity at various temperatures up to the melting-point. The experimental difficulties, though great, should not be insuperable.

II. *Silver.*—About 400 grm. of silver were used. A good mirror was easily prepared, but lost its polish on heating to redness, reflecting light from the furnace walls, and preventing measurement of the true emissivity. This instability of the surface was noted by Drude, even when the metal was heated in hydrogen. It is perhaps connected with the noticeable volatility of the metal.

The emissivity of a clear surface of liquid silver was, however, measured. The results are tabulated below, along with Hagen and Rubens' (*loc. cit.*, p. 16) directly and Minor's (*loc. cit.*, p. 614) indirectly obtained values for the absorptivity (1 − R) of solid silver mirrors.

Table II.

Wave-length in $\mu\mu$.	Relative emissivity of liquid silver.				Absorptivity of solid silver.	
	1004°.	1060°.	1117°.	Mean.	Hagen and Rubens.	Minor.
700	—	6·66	7·22	6·99	5·4	—
675	—	6·90	7·41	7·15	—	—
650	6·87	7·22	7·30	7·18	6·5	—
625	6·77	6·97	7·37	7·09	—	—
600	7·03	7·17	7·58	7·31	7·4	5·0 (for 589·3 $\mu\mu$)
575	7·39	7·75	7·74	7·67	—	—
550	7·77	8·06	8·27	8·09	7·3	5·8
525	7·63	8·49	9·03	8·53	—	—
500	—	8·17	9·48	8·82	8·7	6·8
450	—	—	—	—	9·5	8·3

The relative emissivity of liquid silver is shown graphically in the diagram. Since the reflectivity of silver is very high, a small error in its determination would involve a large error in the absorptivity, as given above; because of this uncertainty the values for the absorptivity are not shown graphically. It will be seen that the relative emissivity of the liquid is throughout somewhat greater than the absorptivity of the solid. There is no other remarkable feature about the emissivity of liquid silver, except its extreme smallness throughout the visible spectrum, as might be anticipated from the high reflectivity of the metal. This lowness of emissivity made measurements, especially near the melting-point, very difficult; it is therefore doubtful

whether the apparent slight increase in relative emissivity with rise in temperature, shown in the table, is real. On this account also only half weight is given to the measurements at 1004°, in calculating the mean.

As in the former paper for gold, it is thought of interest to calculate the "black body" temperature, S, of the metals at their respective melting-points.

Table III.—"Black Body" Temperature of Copper and Silver at their Melting-Points.

Wave-length in $\mu\mu$.	Copper. Melting-point 1083·4° C.		Silver. Melting-point 960·7° C.
	S (solid) in °C.	S (liquid) in °C.	S (liquid) in °C.
700	896	917	792
675	912	928	799
650	924	942	804
625	943	956	808
600	966	973	816
575	988	989	823
550	1007	1003	831
525	1018	1015	838
500	1028	1026	845
475	—	1033	—

Summary.

1. The emissivity of solid and liquid copper and of liquid silver at high temperatures, relative to that of a full radiator at the same temperatures, has been measured throughout the visible spectrum.

2. As in the case of gold, the emissivity of copper is discontinuous at the melting-point, the "relative emissivity" curve of the liquid showing no flexure.

3. The curve of "relative emissivity" of solid copper at high temperatures differs considerably from that of absorptivity at low temperatures; it possesses a much less marked flexure in the green, and it is suggested that this is due to the same causes which ultimately bring about the total absence of a marked bend in the curve for the liquid.

4. Contrary to Burgess's results, no appreciable temperature coefficient of "relative emissivity" was found for liquid copper over a range of 100°.

5. The "relative emissivity" of liquid silver is throughout remarkably low, but seems to be somewhat greater than the corresponding values of the absorptivity of solid silver at ordinary temperatures.

6. "Black body" temperatures of solid and liquid copper and of liquid silver at the respective melting-points are calculated.

The author desires to express his thanks to Prof. F. G. Donnan for his advice and help, and to Mr. L. Spencer for his invaluable assistance in making some of the measurements.

On the Spontaneous Crystallisation and the Melting- and Freezing-point Curves of two Substances which form Mixed Crystals and whose Freezing-point Curve exhibits a Transition Point.—Mixtures of p-*Bromnitrobenzene and* p-*Chlornitrobenzene.*

By Miss FLORENCE ISAAC.

(Communicated by Sir Henry A. Miers, F.R.S. Received January 18,—Read January 30, 1913.)

The following paper is a continuation of two previous papers in which the melting- and freezing-point curves for two pairs of substances, each of which forms mixed crystals, have already been determined.

In the first of these papers* mixtures of naphthalene and β-naphthol were examined and found to form a continuous series of mixed crystals and to give curves of Roozeboom's Type I, in which the melting and freezing points of all mixtures lie between the melting points of the pure substances.

In the second paper† mixtures of azobenzene and benzylaniline were examined and found to form mixed crystals of two kinds, whose melting- and freezing-point curves exhibit a minimum or eutectic point (Roozeboom's Type V).

The present paper deals with mixtures of a pair of substances—*p*-bromnitrobenzene and *p*-chlornitrobenzene—which form mixed crystals and give freezing-point and melting-point curves belonging to Type IV of Roozeboom, in which, though the melting and freezing points of all the mixtures lie between those of the pure substances, the curves show a break or discontinuity corresponding to the existence of two kinds of mixed crystals, as in Type V.

* 'Journ. Chem. Soc.,' 1908, vol. 93, I, p. 927.

† 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 344.

Mixtures of *p*-bromnitrobenzene and *p*-chlornitrobenzene have already been studied by Kremann* in a paper on isomorphous mixtures. This author has traced the freezing-point curve for mixtures of these substances, and has shown that they form mixed crystals, and he also obtained five points lying on the melting-point curve.

Kremann obtained his freezing- and melting-point curves from observations made on the rate of cooling of various mixtures. Liquid mixtures of known composition were allowed to cool, and a curve was obtained for each mixture by plotting temperature against time. It was found that these cooling-curves showed two distinct kinks, one when crystallisation commenced and the second at what Kremann describes as the end of crystallisation. From these cooling-curves Kremann obtained his freezing- and melting-point curves for the mixtures, the freezing-point curve or liquidus being given by the upper kinks, at which crystallisation started in the various mixtures, and the melting-point curve or solidus being given by the lower kinks, at which Kremann states that crystallisation ends. In this manner he obtained curves of Roozeboom's Type IV.

Since, however, he only obtained five points on the melting-point curve, none of which lie in the neighbourhood of the transition point, his curve is to some extent imaginary. The following experiments were therefore undertaken with a view to verifying his results, and to determining a more complete set of melting points, and also in order to obtain the supersolubility curve or curve of spontaneous crystallisation for a series of mixtures of Roozeboom's Type IV, in the same manner that this curve has already been obtained for mixtures of naphthalene with β-naphthol, and azobenzene with benzylaniline, which afford examples of Type I and Type V respectively.

Crystalline Form of p-*Bromnitrobenzene and* p-*Chlornitrobenzene.*

Crystals of *p*-bromnitrobenzene have been examined by Fels,† who describes them as melting at 126° or 127°, and having a specific gravity of 1·934 at 22°, and states that *p*-bromnitrobenzene is isomorphous with *p*-chlornitrobenzene. He obtained, from a solution in a mixture of acetone and ether, crystals which were colourless or slightly yellow, prismatic in the direction of the *c*-axis, and showing only *n* {210} and *c* {001}. He found the crystals to be monoclinic, having

$$a : b : c = 1{\cdot}9336 : 1 : \ ? \ ; \qquad \beta = 97^\circ\ 57'.$$

* 'Jahrb. der k. k. Geol. Reichsanstalt,' 1908, vol. 58, p. 659.

† 'Zeitschr. für Kryst. u. Min.,' 1900, vol. 32, p. 375.

The extinction on a prism face was 22°. He also states that a crystal of *p*-bromnitrobenzene will continue to grow when placed in an alcoholic solution of *p*-chlornitrobenzene, and that crystals of the latter which form in the neighbourhood will arrange themselves parallel to the *p*-bromnitrobenzene crystal introduced.*

p-Bromnitrobenzene has also been examined by Kekulé,† who describes the crystals as needles having melting point 125°; and by Fittig,‡ who describes the crystals as long colourless needles, fine as a hair, slightly soluble in cold alcohol, and having melting point from 126° to 127°.

Fels also examined *p*-chlornitrobenzene§ and obtained the melting point of this at 83° to 84°, and its specific gravity as 1·520 at 18°.

He found the crystals to be monoclinic, having

$$a : b : c = 1{\cdot}9577 : 1 : 1{\cdot}1203; \qquad \beta = 97° \; 11',$$

the plane of the optic axes being (010). The crystals were colourless and prismatic in habit, showing the forms $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{10\bar{1}\}$. When grown from alcohol they usually showed as end faces only $\{10\bar{1}\}$, whilst those grown from ether, acetone, or benzene showed the form $\{001\}$. Since the crystals become dull quickly in the air, Fels states that the reflections are always poor. The extinction angle on a prism face was here 16·5°. *p*-Chlornitrobenzene has also been examined by Jungfleisch,‖ who obtained it in the form of large plates derived from a rhomboidal prism of 125½°, but without end faces.

Microscopic Examination of p-*Bromnitrobenzene*, p-*Chlornitrobenzene, and their Mixtures.*

No goniometric measurements of *p*-bromnitrobenzene and *p*-chlornitrobenzene were undertaken, but both substances were examined under the microscope while growing from solution on a microscope slide.

p-Bromnitrobenzene, dissolved in a drop of alcohol, ether, or benzene on a slide under a cover-glass, gave fine feathery needles branching in all directions. The needles showed no end faces, so no angles could be measured. The extinction was inclined at 18° or 20° to the length of the needles. In convergent light no optic axis could be seen, but only a dark brush crossing the field as the nicols revolved.

p-Chlornitrobenzene dissolved in a drop of benzene, alcohol, toluene, or

* An attempt to confirm this observation did not lead to any positive result.

† 'Liebig's Annalen der Chemie,' 1866, vol. 137, p. 167.

‡ 'Ber. deutsch. Chem. Ges.,' 1874, vol. 7, p. 1175.

§ 'Zeitschr. für Kryst. u. Min., 1900, vol. 32, p. 375.

‖ 'Ann. de Chimie et de Phys.,' 1868 (4), vol. 15, p. 223.

acetone, gave under the same conditions crystals which grew in a feathery manner in long branching needles having straight extinction. These needles had no end faces and therefore no measurable angles. Examined in convergent light these needles showed an optic axis visible on the edge of the field. The birefringence is positive, and the plane of the optic axes along the length of the needles. This would correspond to the different habit of the two substances noted by Fels, the face *a* being only found on the chloro-compound.

A few experiments made with mixtures of these substances under the microscope yielded somewhat indefinite results, no angular measurements being possible since the crystal needles had no end faces, but they seemed to show that mixtures containing up to 27·5 per cent. of *p*-bromnitrobenzene gave crystal needles showing the same straight extinction and the same optic axial figure as pure *p*-chlornitrobenzene. Mixtures having more than 27·5 per cent. of *p*-bromnitrobenzene, on the other hand, gave crystal needles having the oblique extinction (about 20°) of pure *p*-bromnitrobenzene, and they also show no optic axis when viewed in convergent light. These experiments would indicate therefore that a change of some sort probably occurs in the crystals growing from these mixtures at the composition 27·5 per cent. *p*-bromnitrobenzene, 72·5 per cent. *p*-chlornitrobenzene, and subsequent experiments to be described in this paper show that at this composition there is a break or change in direction in the freezing-point curve, which would indicate a change in the nature of the crystals.

The Freezing-point Curve.

Mixtures of *p*-bromnitrobenzene and *p*-chlornitrobenzene were examined in sealed glass tubes, and the freezing point for each mixture was obtained by the method which has been already employed by the author in the papers referred to above. Each tube was heated in an oil bath with glass windows until the contained mixture was completely melted; it was then held outside the bath a few seconds to induce one or two small crystals to start growing. The tube was then re-immersed in the oil bath and these small crystals watched while the temperature of the bath was varied until a temperature was attained at which equilibrium existed between the liquid and the small crystals, and this was taken as the freezing point of the mixture.

The following are the tabulated results obtained for the freezing points of the various mixtures examined :—

Percentage by weight of *p*-bromnitrobenzene in the mixture.	Freezing point.	
	°	
100·0	124·0	
90·016	119·4	
79·886	115·2	
75·175	112·8	
70·0	110·8	
64·888	107·5	
59·874	104·8	
54·645	101·5	
45·22	96·75	
44·855	96·3	
40·339	93·8	
37·747	92·2	
32·849	89·5	
29·952	87·7 (β)	84·5 (α)
29·915	87·7 (β)	84·5 (α)
27·478		84·5
25·041		84·5
19·94		84·2
14·957		83·8
14·935		83·8
9·972		83·0
5·024		82·8
0		82·0

It will be seen that for mixtures containing about 30 per cent. of *p*-bromnitrobenzene two freezing points have been obtained for the same mixture. These correspond to two different sorts of mixed crystals, α and β, two kinds being distinctly visible and having different melting points, at 87·7° and 84·5° respectively. The crystals α, growing in the liquid mixture at the lower temperature (84·5°), are wide, transparent, quickly growing blades, and occur in all the mixtures having less than 30 per cent. of *p*-bromnitrobenzene. The crystals β, which are in equilibrium with the liquid at 87·7°, are extremely fine small hair-like needles, growing very slowly. In all mixtures containing over 30 per cent. of *p*-bromnitrobenzene, these very fine hair-like crystals only are to be seen. Both sorts of crystals, α and β, may be found also in a liquid mixture containing 27·5 per cent. of *p*-bromnitrobenzene, but in this case they are both deposited at the same temperature and the existence of two sorts is therefore not so noticeable. At this point, corresponding to 27·5 per cent. of *p*-bromnitrobenzene, it will be seen that the freezing-point curve shows a break or transition point. For mixtures containing above 27·5 per cent. of *p*-bromnitrobenzene the freezing-point curve rises much more rapidly than for mixtures containing a smaller percentage, the curve for mixtures containing between 0 per cent. and 27·5 per cent. of *p*-bromnitrobenzene being very flat and only rising by 2·5°.

It is to be expected that in the neighbourhood of this transition point the melting-point curve also will show discontinuity.

Comparing the values here obtained for points on the freezing-point curve with those observed by Kremann it will be seen that the new values are throughout somewhat higher than the old ones, although Kremann's transition point was found to correspond to a mixture of almost the same composition as that obtained above. Thus Kremann's freezing points for mixtures with 100, 70·8, 39·6, and 23·1 per cent. of *p*-bromnitrobenzene are 123°, 108°, 91·5°, and 84·5° respectively; while the values here obtained for mixtures of the same composition are 124°, 111°, 93·3°, and 84·3° respectively. This discrepancy may probably be due to slight supercooling having taken place before the first separation of crystals in Kremann's cooling experiments.

The Melting-point Curve.

The freezing-point curve having been determined, an attempt was now made to fix the position of the melting-point curve for the same mixtures.

The method used was the same as that adopted in the case of mixtures of azobenzene and benzylaniline already referred to (*loc. cit.*, p. 349). The same tubes of mixtures were, for the most part, used that had been used to determine the freezing-point curve. The mixtures were heated until they were completely liquid, and they were then allowed to cool slowly in the bath until they had completely recrystallised, the crystals adhering to the sides of the tubes. At least 24 hours were allowed, to enable the mixtures to solidify completely. They were then heated again very steadily in the oil bath, and as the temperature rose the crystals were examined continually with a lens, until, when it had reached a certain point, some of the crystals in the tube began to look slightly sticky, and a further rise in the temperature of about half a degree caused a small stream of liquid to run down the sides of the tube. The point at which melting was first observed was taken as the melting point of the mixture. This method of obtaining the melting-point curve for mixed crystals has also been used by A. Stock.* This method may be expected to give satisfactory results in fixing the melting-point curve or solidus, since, according to the theory, when mixed crystals grow from a liquid mixture the crystals first deposited differ in composition from the original liquid; but if solidification proceeds with sufficient slowness, the crystals approximate, as the temperature falls, more and more nearly in composition to the original liquid taken, until finally the last crystals which form should have the exact composition of the original liquid. The method was found to give satisfactory results in the case of mixtures of azobenzene and benzyl-

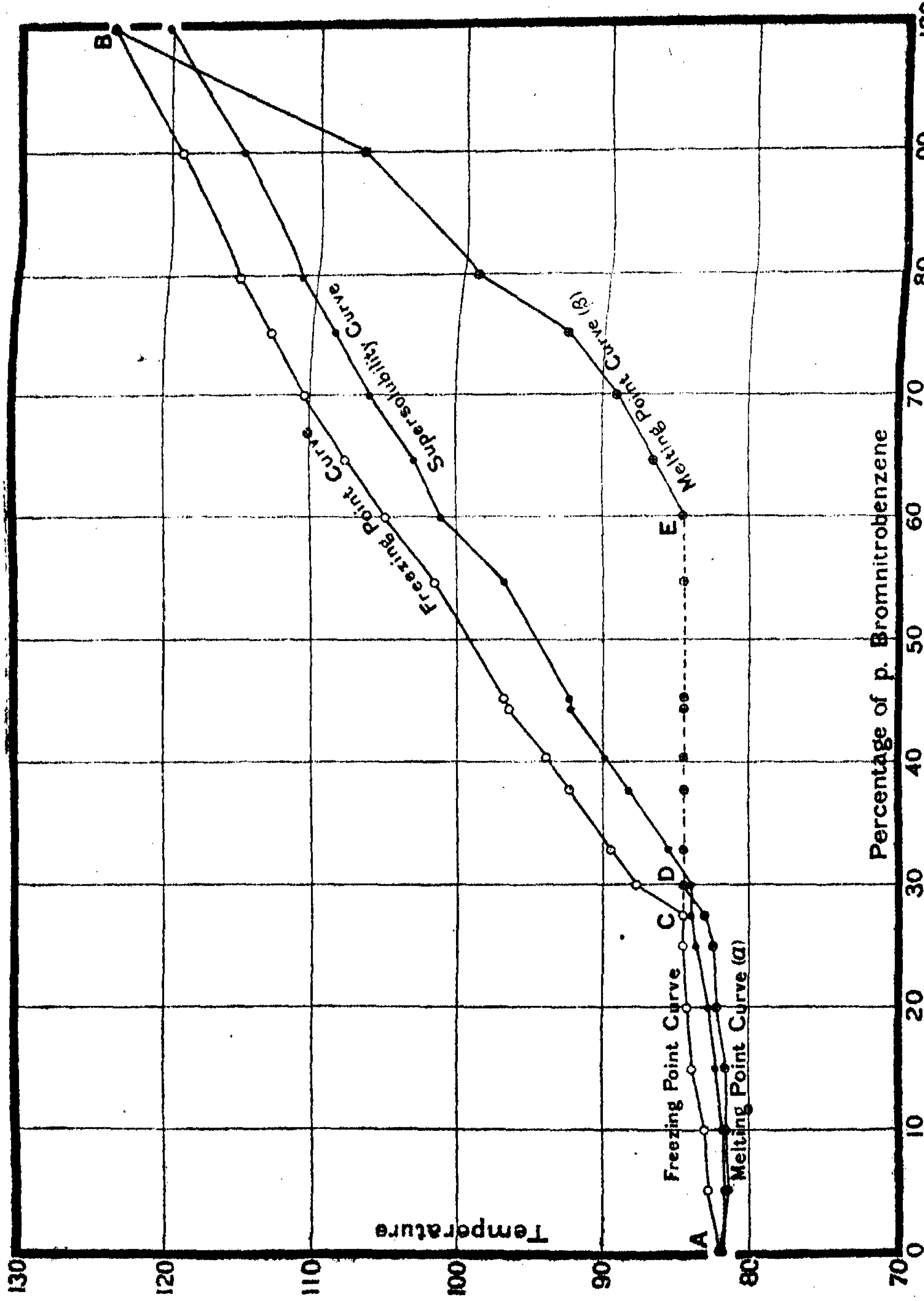
* 'Ber. deutsch. Chem. Ges.,' 1909, vol. 42, p. 2059.

aniline, the curve obtained in this manner being confirmed by actual analysis of the mixed crystals (*loc. cit.*, p. 352). The method, therefore, having been tested, there is no reason to doubt that the results described below for the melting-point curves of mixtures of *p*-bromnitrobenzene and *p*-chlornitrobenzene are very approximately correct. All the determinations have been very carefully made and each been repeated several times with concordant results.

The following table gives the melting points obtained:—

Percentage by weight of *p*-bromnitrobenzene in the mixture.	Melting point.
	°
100·0	124·0
90·016	107·0
80·033	99·0
75·175	92·5
70·0	89·0
64·690	86·5
59·874	84·5
54·645	84·5
45·22	84·5
44·355	84·5
40·339	84·5
37·747	84·5
82·849	84·5
29·952	84·5
29·915	84·5
27·478	83·0
25·041	82·4
19·94	82·2
14·957	81·5
9·972	81·5
5·024	81·4
0	82·0

The melting-point curve plotted from these figures appears in the diagram. Examination of the complete figure formed by the freezing- and melting-point curves for these mixtures shows that they form an example of Roozeboom's fourth type of curves for mixed crystals. The two branches AC and CB of the freezing-point curve or liquidus have each a corresponding melting-point curve or solidus, AD and EB respectively. At the temperature 84·5° of the transition point C, two solid phases, α and β, may exist in equilibrium with the liquid containing 27·5 per cent. of *p*-bromnitrobenzene and 72·5 per cent. of *p*-chlornitrobenzene. These two solid phases will contain respectively 30 and 60 per cent. of the bromo-compound. C is therefore an invariant point, and the transition from one series of crystals to the other, indicated by the horizontal line CDE, takes place at constant temperature. All liquid mixtures to the left of C solidify



as α-crystals, and all liquid mixtures to the right of E solidify as β-crystals Mixtures between D and E first form some β-crystals and then α-crystals,

which will have the compositions E and D respectively. Varying the composition of the liquid between the limits D and E will change only the relative proportion of the two phases, α and β, without altering the composition of either. Mixtures between C and D also first form β-crystals, but on cooling slightly past the transition point these are all converted into α-crystals.

It has been seen that for mixtures containing 0 to 27·5 per cent. of *p*-bromnitrobenzene the rise of temperature in the freezing-point curve is very slight, viz. only 2·5°. According to the theory of mixed crystals of Roozeboom's Type IV, addition of *p*-bromnitrobenzene should raise the melting point of the mixture. It may be seen, however, that for mixtures containing from 5 to 15 per cent. of *p*-bromnitrobenzene the melting points of the mixtures are actually slightly lowered by the addition of *p*-bromnitrobenzene. The lowering is, however, very slight, amounting nowhere to more than 0·6°. This slight lowering cannot be accounted for otherwise than by the assumption that one or both of the substances may contain some small quantity of impurity. The melting points obtained for them, namely 124° and 82°, seem to indicate that this may be the case, since Fels obtained 126° to 127° as the melting-point of *p*-bromnitrobenzene, and 83° to 84° as the melting point of *p*-chlornitrobenzene.

Comparing the results here obtained for the melting-point curve with the five melting points obtained by Kremann it will be seen that there is a wide discrepancy in the results.

Percentage by weight of *p*-bromnitrobenzene in the mixture.	Melting point.	
	Kremann.	Isaac.
	°	°
83·7	111·0	101·0
70·3	108·0	89·0
56·1	100·0	84·5
46·1	94·8	84·5
24·2	84·3	82·0

It would appear, therefore, from the above values that Kremann's melting points, obtained from the second kink in the cooling-curves for mixtures, are too high; and this would seem to indicate that the mixtures could not have been completely solid at the time this second kink in the cooling-curve appears. In the experiments described in this paper it has been found that the mixtures cannot be regarded as completely solid until several hours after the crystals first appeared in the liquid; and, as stated

above, at least 24 hours were allowed to elapse before the melting point of any mixture was taken.

The Spontaneous Crystallisation of Mixtures of p-*Bromnitrobenzene and* p-*Chlornitrobenzene.*

Finally, the methods described in the previous papers have been applied to mixtures of *p*-bromnitrobenzene and *p*-chlornitrobenzene, in order to trace their supersolubility curve or curve of spontaneous crystallisation. The mixtures were enclosed in sealed glass tubes which also contained some fragments of corundum to produce friction, and the tubes were heated for some time in the oil bath and shaken thoroughly as the temperature of the bath was raised, until all trace of solid had disappeared. After heating further to at least 10° above the freezing-point curve the temperature of the bath was allowed to fall very slowly, the oil being constantly agitated in order to keep its temperature uniform throughout. Thermometers placed at top and bottom of bath showed this to be the case. The tube containing each of the liquid mixtures was shaken continuously (by hand) in the bath as the oil cooled, until at a certain temperature a shower of very fine crystal needles suddenly appeared in the tube, and thickened very rapidly until the whole tube was opaque. The temperature at which crystals first appeared in each tube was noted as the temperature of spontaneous crystallisation for that mixture. The results are tabulated below, and from

Percentage by weight of *p*-bromnitrobenzene in the mixture.	Temperature of spontaneous crystallisation.
	°
100·0	120·2
90·016	115·1
79·886	111·0
75·175	108·3
70·0	105·3
64·888	102·8
59·874	101·0
54·645	96·7
45·22	92·3
44·355	92·2
40·339	89·8
37·747	88·2
32·849	85·5
29·915	84·0
27·478	84·0
25·041	83·4
19·94	82·7
14·957	82·2
14·935	82·1
9·972	81·8
5·024	81·7
0	81·7

them the complete supersolubility curve is obtained which is shown on the diagram.

The goniometric method of plotting the supersolubility curve from observations of the refractive index, which was used in the research on mixtures of azobenzene and benzylaniline, was not used for the present mixtures, since the high temperatures at which they crystallise render them unsuitable for use in the goniometer trough.

An examination of the supersolubility curve as it appears on the diagram shows that it, too, exhibits a break or bend for mixtures containing from 27·5 per cent. to 30 per cent. of *p*-bromnitrobenzene, corresponding to the transition point on the freezing-point curve. It follows the direction of the freezing-point curve very closely, lying about 4° below it on the right-hand side of the transition point, and about $1\frac{1}{2}$° below on the left-hand side of that point. It lies entirely above the melting-point curve except just at both the extreme ends, when it crosses it.

In a paper by Vanstone* the author states that the freezing-point curves as usually obtained for mixed crystals from the rate of cooling are in reality the temperatures of spontaneous crystallisation. This suggests that Kremann's freezing-point curve, obtained from observations of the cooling-curves, might coincide with the supersolubility curve here obtained. Comparison with Kremann's figures shows, however, that his freezing-point curve lies between the freezing-point curve and the supersolubility curve, though on the whole it lies slightly nearer to the latter. Thus it would appear that in Kremann's experiments crystallisation started in a supersaturated mixture, but before the mixture actually arrived at the labile temperature. This is what might have been expected, unless special care were taken to prevent inoculation of the mixture by a crystal germ, by enclosing the mixtures in sealed tubes or other means.

The bath used in all these experiments consists of a square-shaped copper vessel of sufficient depth to allow the sealed glass tubes to be completely immersed. It was filled with cotton-seed oil and heated by means of a Bunsen burner placed immediately beneath it. Two round plate-glass windows were inserted in the sides of the bath immediately opposite each other, and held in place by means of brass rings and screws. The bath was illuminated by means of a ground-glass electric bulb placed behind one of the windows, and the crystals were examined as they grew in the tubes with a lens held at the opposite window.

* 'Journ. Chem. Soc.,' 1909, vol. 95, I, p. 599.

Conclusions.

The results obtained in this paper may be briefly summarised.

1. *p*-Bromnitrobenzene, *p*-chlornitrobenzene and their mixtures have been optically examined under the microscope.

2. The freezing- and melting-point curves for these mixtures have been determined. It has been found that these substances form mixed crystals and give curves of Roozeboom's Type IV. The freezing-point curve shows two branches corresponding to two different sorts of mixed crystals and meeting in a transition point at 84·5°, for a mixture containing 27·5 per cent. of *p*-bromnitrobenzene and 72·5 per cent. of *p*-chlornitrobenzene. The freezing-point curve was found to correspond very nearly to that already obtained by Kreeman for these mixtures, though Kremann's curve lies somewhat below it. The melting-point curve also shows two branches, corresponding to the two branches of the freezing-point curve, and on each of these a different kind of mixed crystal is in equilibrium with the liquid. At the temperature marked by the dotted horizontal line, both sorts of mixed crystals may exist together in equilibrium with a liquid containing 27·5 per cent. of *p*-bromnitrobenzene. The melting-point curve here obtained differs widely from that obtained by Kremann, a large part of the curve lying considerably below the latter.

3. The supersolubility curve or curve of spontaneous crystallisation has been determined for these mixtures, and it has been found that each mixture possesses a definite temperature of spontaneous crystallisation. This curve lies almost completely between the melting- and freezing-point curves, and, like them, it shows a break in the neighbourhood of the transition point.

My sincere thanks are due to Prof. H. L. Bowman for his kind help and interest throughout this research.

The Excitation of γ-Rays by the α-Rays of Ionium and Radiothorium.

By J. Chadwick, M.Sc., Beyer Fellow of the University of Manchester, and A. S. Russell, M.A., Carnegie Research Fellow of the University of Glasgow.

(Communicated by Prof. E. Rutherford, F.R.S. Received January 25,— Read February 13, 1913.)

Introduction.

It has been shown by one of us* that the α-rays of radium C, when they impinge upon matter, excite a small but detectable amount of γ-radiation. Owing to the presence of the intense primary γ-radiation which accompanies the α-rays of radium C, however, a detailed investigation of this excited γ-radiation was not possible. With an intense source of ionium placed at our disposal by Prof. Rutherford it has been possible for us, not only to show clearly that γ-rays are excited by the α-rays of ionium, but also, owing to the absence of products emitting β- and γ-rays, to make a detailed study of the nature of this excited γ-radiation. The results of these experiments are given in this paper. We have found also that γ-rays are emitted from radiothorium, and a short account of the work which led to this result is given here also, although, as will be explained later, it was not possible for us to make a systematic study of their nature.

The γ-Rays from Ionium.

The preparation of ionium used in these experiments consisted of a mixture of the oxides of thorium and ionium separated by Prof. Boltwood from the "actinium residues" loaned by the Royal Society to Prof. Rutherford. Its activity was such that 1 grm. expelled 1×10^8 α-particles per second, *i.e.* 1 grm. of the mixture contained a quantity of ionium equivalent to the amount of ionium in radioactive equilibrium with 3 mgrm. of radium. The quantity of oxide used in most of the experiments weighed 1·2 grm.

It is obvious that if definite evidence of the existence of γ-rays from ionium is required, the ionium in the mixture must be freed from every trace of bodies which emit β- or γ-radiations. Besides thorium and ionium, the preparation contained all the products of the thorium series, and, in addition, radium and its products. The radium had, of course, been grown

* Chadwick, 'Phil. Mag.,' 1913, vol. 25, p. 193.

from the ionium in the two years that had elapsed since its last purification. Measurement of the $(\beta+\gamma)$-ray activity of the preparation previous to its purification showed that it had an activity of 200 divisions per minute under the experimental conditions, and this was doubtless mainly due to the radium C present.

All products emitting β- and γ-rays were freed from ionium by the following series of chemical operations. The preparation was fused in small portions with potassium bisulphate in a platinum crucible. The fused masses were powdered and dissolved in hot water. From this solution the ionium and thorium were precipitated as hydroxides by the addition of ammonia. The hydroxides were dissolved in acid and reprecipitated by ammonia, this operation being repeated. These operations separate radium, mesothorium 1, and thorium X completely from the ionium. The hydroxides were then dissolved in acid, and ammonia added until its further addition would produce a slight precipitate. The ionium and the thorium were precipitated from the clear solution by the addition of meta-nitrobenzoic acid in excess. This frees the ionium from mesothorium 2, radium B, thorium B, and radium D. The precipitate was then ignited. The activity due to β- and γ-rays combined, measured under the same conditions as before purification, was now 13 divisions per minute. The activity remained practically constant for a period of 10 days, showing that it could not be due to radium E or any other of the products of radium. An equal weight of old commercial thorium treated by exactly the same chemical methods, when measured immediately after purification, was found to be quite free from β- and γ-rays. A month later, when the thorium X and its products had been formed in equilibrium amount, the activity due to the β- and γ-rays was only 2 divisions per minute. The $(\beta+\gamma)$-ray activity of the ionium preparation cannot therefore be ascribed to the thorium that it contains.

It was thought not improbable that some unknown product emitting β-rays might have been originally present, and a small portion of it still remained unseparated from the ionium. The preparation was therefore brought into solution as before, precipitated three times with ammonia, and once with meta-nitrobenzoic acid, and finally ignited. It was found that the $(\beta+\gamma)$-ray activity of the preparation had not been changed appreciably by this second series of chemical operations. It was concluded from these experiments that this β- and γ-radiation must be due, either to the ionium itself, or to some unknown product which is chemically very similar to it. A detailed study of the rays was then commenced. A large electroscope of the ordinary type, 17 cm. × 17 cm. × 17 cm., was placed immediately above

the pole pieces of a very powerful electromagnet. The base of the electroscope was of lead in which was cut an opening 10 cm. × 10 cm., covered by very thin aluminium foil. The faces of the pole pieces were 10 cm. × 16·5 cm., and 9 cm. apart. They were covered with thick cardboard to minimise diffuse reflection of β- and γ-rays from them. The active material was placed between the pole pieces at a distance of 9 cm. below the base of the electroscope. It was in the form of a film spread evenly over an area of about 15 sq. cm. on a shallow platinum dish. Under these conditions the leak in the electroscope due to β- and γ-rays was 13·3 divisions per minute. When a magnetic field of about 1000 gauss was applied, the leak in the electroscope was 12 divisions per minute. The $(\beta+\gamma)$-ray activity of a film of uranium oxide, measured under the same conditions, was reduced by the same magnetic field to less than 1 per cent. The activity of 12 divisions per minute due to the ionium preparation must therefore be due to γ-rays. Only 10 per cent. of the total activity can be due to β-rays, and this small amount may be due entirely to β-rays from thorium products, though probably part at least is due to the ionium.

It is interesting to note that Boltwood,* the discoverer of ionium, stated that ionium emitted β-rays as well as α-rays. Keetman† showed, however, that these rays were due entirely to the presence of uranium X, which, being non-separable from ionium, had been separated with it by Boltwood from the mineral. Keetman, working with an ionium preparation comparable in intensity with ours, found no evidence of any radiation more penetrating than α-rays. His failure to detect the γ-rays must be ascribed to lack of sensitiveness of his methods of measurement. The amount of γ-radiation from ionium is very small, and of quite a different order, relative to the amount of α-radiation, from that of a product emitting both α- and γ-rays such as radium C. The amount, however, is of the same order as that excited by the α-rays of radium C when they impinge upon matter. Not only is the value of the γ to α ratio abnormally low, but the γ to β ratio is abnormally high. The ratio of the ionisations due to the γ- and the β-rays from a radio-element in an ordinary electroscope is in the most favourable case 1/50. In the case of ionium this ratio is at least 10. The existence of a new product, therefore, emitting γ- and β-rays in this proportion, and chemically difficult to separate from ionium, is in the highest degree improbable. For these reasons it must be concluded that the γ-rays from ionium are excited by the α-rays, either in the ionium itself, or in the surrounding atoms of thorium.

* Boltwood, 'Amer. Journ. Sci.,' 1906, vol. 22, p. 537.

† Keetman, 'Jahr. Radioaktivität,' 1909, vol. 6, p. 269.

Absorption Measurements in Aluminium.

In all the experiments to be described, except where the contrary is stated, measurements were conducted with a magnetic field applied to deflect from the electroscope the β-rays emitted by the preparation. The absorption curve of the γ-rays has been carefully determined from 0 to 5 cm. of aluminium. The curve for the whole range is shown in fig. 1. It can readily be seen that the curve consists of three different parts. The first part, AB, shows the existence of a very soft type of radiation which is totally absorbed by 0·003 cm. of aluminium, the second, BC, of a harder type which

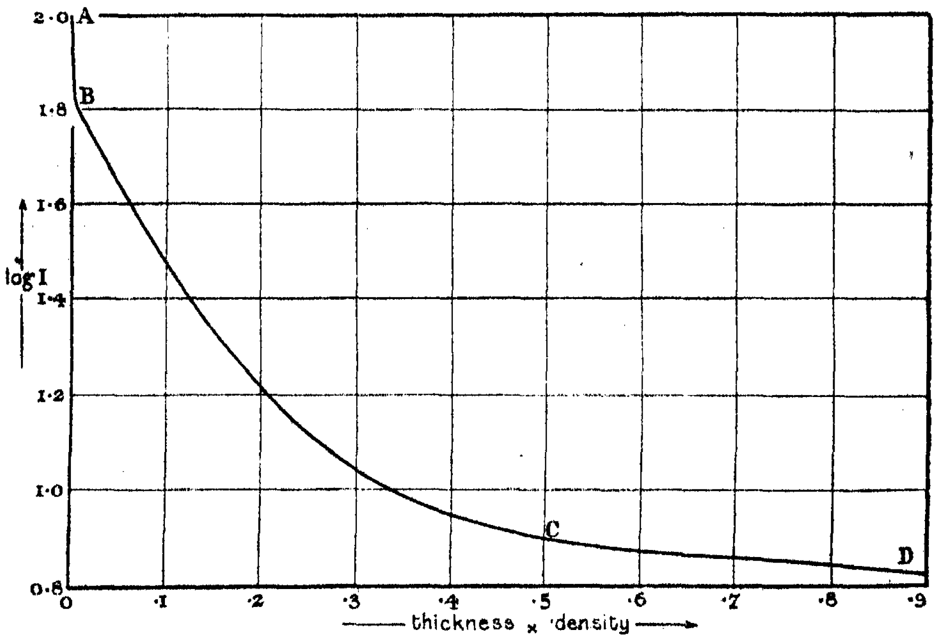


FIG. 1.

is not detectable after it has passed through 0·5 cm. of aluminium, and the third, CD, of a small amount of a still harder type which can be detected even after it has passed through 4 cm. aluminium. The absorption of each type has been studied separately, and the absorption curves obtained are given in figs. 2, 3, and 4 below.

Absorption of the Softest Type.—The active preparation was placed 9 cm. below the electroscope, and the aluminium used for absorbing was laid directly on the preparation. The sheets were very thin, each weighing 0·00065 grm. per square centimetre. After 12 of these sheets had been laid on, all the softest type of radiation had been completely absorbed. The ionisation is then due to the two remaining types of rays. Measurements

made with more than 12 sheets showed that each of the next few sheets beyond this amount absorbed about 0·03 division per minute. This remaining radiation is really absorbed exponentially, but, owing to the extremely small absorption taking place in so small a thickness, it is approximately linear. It is, therefore, a simple matter to calculate the ionisation due to the rays which penetrate 12 sheets, at any thickness less than 12 sheets. The values of this for the different sheets are given in the third column of Table I below. In the first column is given the number of the sheets used for absorbing, in the second the total ionisation measured, and in the fourth the ionisation due to the softest type alone. From these results a value of mass absorption coefficient (μ/D) in aluminium of about 500 $(cm.)^{-1}$ is obtained. Values deduced from other curves obtained in this way varied from $\mu/D=450$ to $\mu/D=520$.

Table I.

Number of sheets.	Total ionisation.	Ionisation due to penetrating rays.	Ionisation due to softest type only.
0	12·31	8·50	3·81
1	11·13	8·47	2·66
2	10·31	8·44	1·87
3	9·70	8·41	1·29
4	9·23	8·38	0·85
5	8·97	8·35	0·62
6	8·77	8·32	0·45
12	8·14	8·14	0·00

It is apparent from these values of μ/D for the softest type of rays, that a large proportion of these rays must be absorbed in the active material itself, and in the air between the electroscope and the active material. A thin film of a small quantity of the material should, therefore, give an ionisation due to the soft rays large compared with that due to the other types. About 25 mgrm. of the active material, in the form of chloride, was carefully evaporated to dryness in a large platinum dish. The film was about 20 sq. cm. in area. When placed about 2 cm. underneath the base of the electroscope, its activity was 57·6 divisions per minute, 50 of which were due to the soft γ-rays, and the remainder, it was found, due chiefly to β-rays. It is seen from these results that the activity of the soft γ-rays has been increased very much by preparing the substance in a thin film. Because of the proximity of the preparation to the electroscope, the β-rays could not be deflected away from the electroscope. After correcting for their absorption, the absorption curve shown in fig. 2 was obtained. It is seen that it is exponential within the error of measurement. The value of μ/D obtained from this experiment

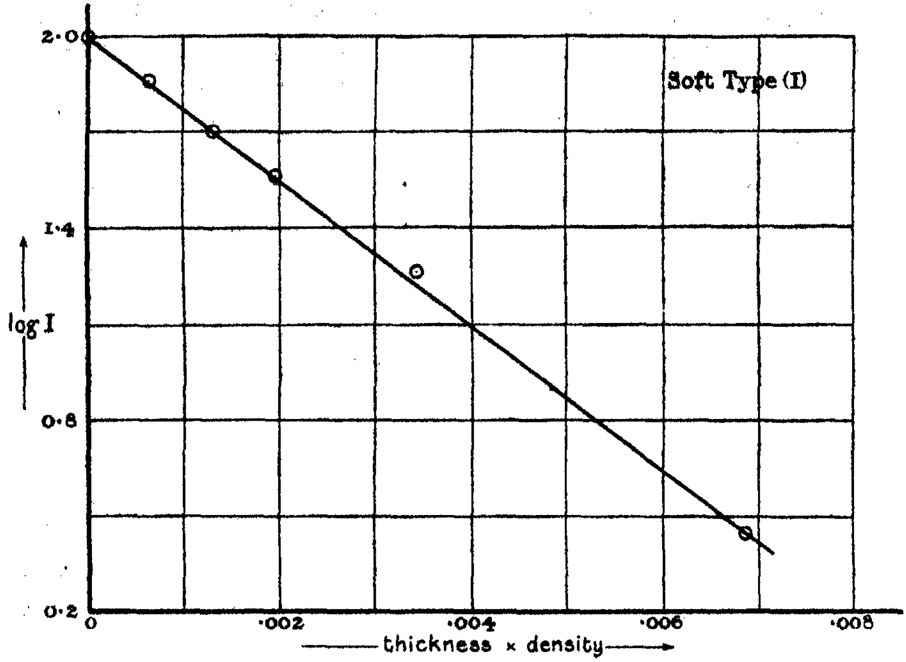


FIG. 2.

was 520 (cm.)$^{-1}$. The leak due to these soft rays measured, not under these special conditions, but at a distance of 9 cm. from the electroscope, as mentioned above, was 3·8 divisions per minute, *i.e.* 32 per cent. of the total ionisation.

Absorption of the Hardest Type.—The absorption of the hardest type of radiation was determined very carefully over a range of thickness of 1 to 5 cm. aluminium. The leak due to this radiation if unabsorbed by aluminium was only 0·94 division per minute, so that the determination of the absorption coefficient is by no means easy. The absorption curve is shown in fig. 3. It is seen that the absorption is exponential. The value of μ/D obtained from the curve is 0·17 (cm.)$^{-1}$.

Absorption of the Rays of Medium Penetrating Power.—The absorption curve of this type of radiation was determined over a range of thickness from that necessary to absorb the softest type totally, to a thickness of 2 mm., beyond which, as further measurements showed, the hardest type alone could be detected. The amount of ionisation, due to the hardest type after traversing any thickness within this range, could be calculated from the data given in the last paragraph. By making the necessary corrections, the ionisation due to the rays of medium penetrating power alone was easily obtained for any thickness, and from these results the curve shown in fig. 4 was plotted. The

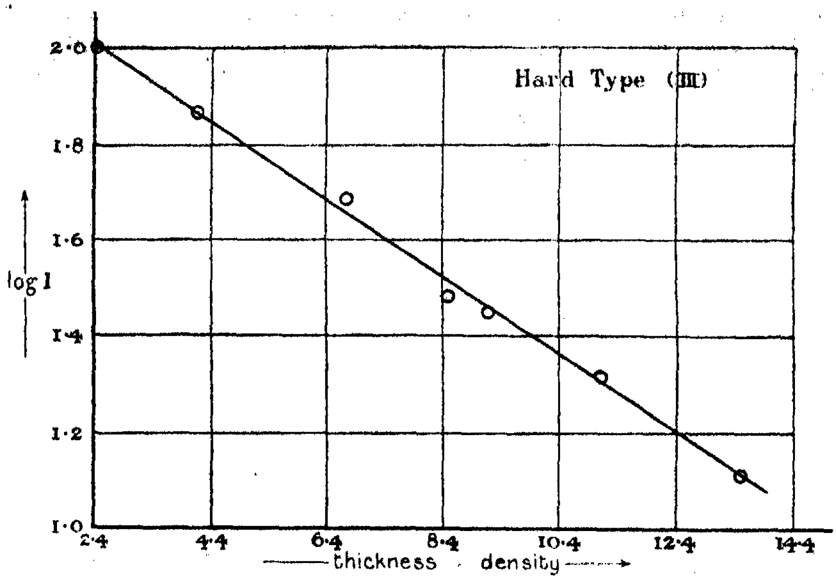

Hard Type (III)
2·0
1·8
1·6
log I
1·4
1·2
1·0
2·4
4·4
6·4
8·4
10·4
12·4
14·4
thickness · density

Fig. 3.

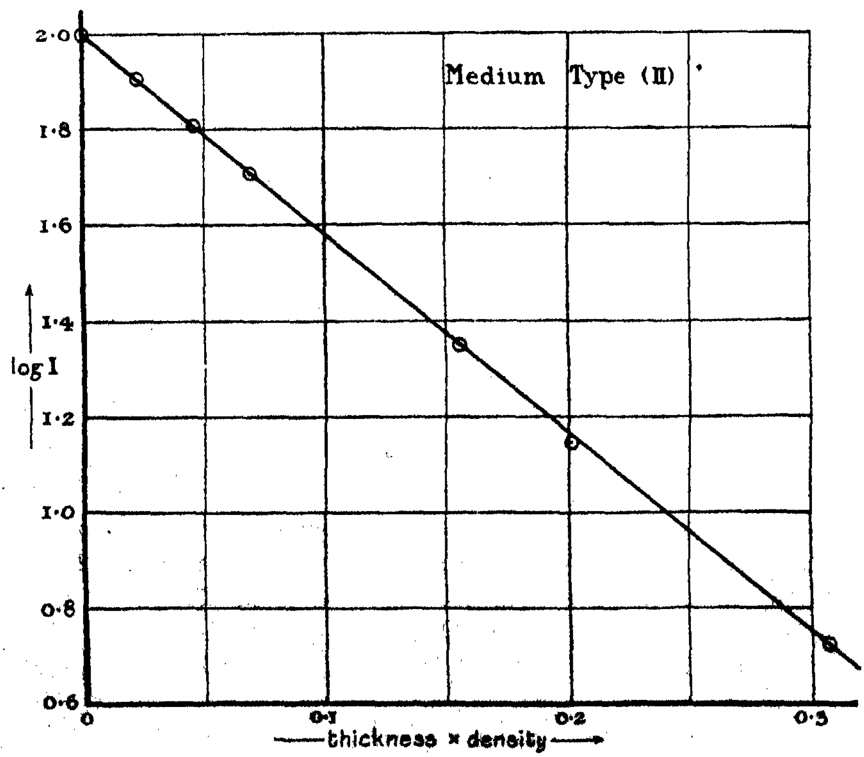

Medium Type (II)
2·0
1·8
1·6
1·4
log I
1·2
1·0
0·8
0·6
0
0·1
0·2
0·3
thickness × density

Fig. 4.

value of μ/D derived from the curve is 9·4 (cm.)$^{-1}$. The leak due to this radiation, when unabsorbed by aluminium, was in the standard disposition 7 divisions per minute, or 60 per cent. of the total ionisation.

Correction for Obliquity of the Beam.—Absorption measurements of γ-rays are usually made under conditions such that the beam of rays under investigation is approximately parallel. In these experiments, however, it was necessary to place the source as near the electroscope as possible, in order to have measurable effects. The values of μ/D given for the three types of rays must therefore be reduced to the values they would have, had the beam been parallel. This can be done by using formulæ derived by Soddy* and by King† from a consideration of the absorption of a cone of rays by a flat plate. If we assume, for simplicity, that the source of γ-radiation is a point source, King shows that if I_t be the ionisation when the rays have penetrated an absorbing plate of thickness t cm., the absorption coefficient of which is μ (cm.)$^{-1}$, I_0 the ionisation of the unabsorbed rays, and 2θ the angle of the cone of rays subtended at the source by the electroscope, then

$$\frac{I_t}{I_0} = \frac{f(\mu t) - \cos\theta\, f(\mu t \sec\theta)}{1 - \cos\theta},$$

where $f(x) = e^{-x} + xEi(-x)$. $Ei(-x)$ is known as the Exponential Integral and is $\int_{-\infty}^{-x} \frac{e^u}{u}\, du$. The mean values of μ/D for the three types of radiation, after correcting for the obliquity of the beam, are given in Table II.

Table II.

Radiation.	(μ/D) (cm.)$^{-1}$ Aluminium.
I. Soft type	400
II. Medium type	8·35
III. Hard type	0·15

It is well known‡ that the value of μ/D for any metal and for any γ-radiation that is absorbed exponentially varies somewhat according to the particular disposition used for measuring the absorption. The γ-rays of radium C, for instance, have a value of μ/D in aluminium of 0·040 when the absorbing material is laid directly over the source and the base of the electroscope is 1 cm. of lead, and 0·0438 when the absorbing material

* Soddy (F. and W. M.) and Russell, 'Phil. Mag.,' 1910, vol. 19, p. 725.

† King, 'Phil. Mag.,' 1912, vol. 23, p. 242.

‡ See Russell, 'Jahr. Radioaktivität,' 1912, vol. 9, p. 444.

is itself the base of the electroscope. The absorption of the hard γ-rays of radium C was therefore investigated under the same conditions as those used for the absorption of the ionium rays. A plate of lead, 1·5 cm. thick, was laid immediately over a source of radium bromide. This absorbs all the soft γ-radiation. Immediately over this lead plate were laid the plates of aluminium. After correcting for the obliquity of the beam the value of μ/D for aluminium was found to be 0·044, which agrees very satisfactorily with the values obtained for ordinary dispositions. The values of μ/D given in Table 2 may therefore be used in making quantitative comparison of the penetrating powers of the rays of ionium with those of X-radiations and γ-radiations, measured in the usual way. No radiation more penetrating than the hard type whose absorption coefficient is given in Table II is given out in detectable amount by the ionium preparation.

Relative Energies of the Three Types of Radiation.

A rough calculation of the relative energies of these three types of radiation has been made. The calculation is necessarily rough, for it involves assumptions which at present, owing to the lack of data, cannot be verified. If we assume, however, that the absorption of any of these types of radiation is, weight for weight, the same in aluminium as it is in air, and secondly, that the ionisation in air is proportional to the absorption, an approximate idea of the relative energies of the three types can easily be obtained. It is probable that neither of these assumptions is strictly true, but it is not likely that they are sufficiently erroneous to lead us to an entirely wrong result. In making the calculation, account must be taken of the absorption in the active material itself, in the air between the material and the base of the electroscope, and in the base of the electroscope. The fraction of the energy spent in ionising the air of the electroscope is readily calculated from the dimensions of the electroscope and the absorbability of the radiation in air.

When the active material, weighing 1·2 grm., and uniformly spread over a surface of 15 sq. cm., was 9 cm. from the electroscope, only 3 per cent. of the total soft γ-radiation escaped from the material. Only 0·93 per cent. of this amount is able to enter the electroscope and produce ionisation. In doing so the radiation is totally absorbed. The ionisation produced was 4 divisions per minute. The total unabsorbed radiation would, therefore, produce $(4 \times 100 \times 100) \div (3 \times 0{\cdot}93)$, *i.e.* 15,000 divisions per minute.

Of the medium type of rays, 68 per cent. emerge from the material; 90·5 per cent. of this amount enters the electroscope, and 16 per cent. of this is absorbed in ionising. The ionisation produced was 7 divisions

per minute. The total unabsorbed radiation would therefore produce $(7 \times 100 \times 100 \times 100) \div (16 \times 68 \times 90{\cdot}5)$, *i.e.* 75 divisions per minute.

Less than 1 per cent. of the hard type is absorbed by the material and the base of the electroscope before it enters the electroscope. Only 0·32 per cent. of the energy is spent in ionisation. Since the leak due to the hard rays was 0·94 division per minute, the total intensity of this radiation is 200 divisions per minute.

It is seen from these figures, obtained for the three different radiations under the same conditions, that 97 per cent. of the total radiation is contained in the soft type (I).

Discussion of Results.

Reasons have been given above for ascribing the production of the γ-rays of ionium to the agency of the α-rays, and an investigation of the penetrating power of the rays has shown that they consist of three different types, varying widely in penetrating power. It now remains to discuss these results in the light of recent work on X-rays and on γ-rays.

Gray* has shown definitely that γ-rays are essentially the same in all properties as X-rays. Recently Rutherford,† from a study of the different types of β-rays emitted by radioactive bodies, has put forward the view that probably the γ-rays of radioactive bodies are the characteristic radiations of these bodies. The characteristic radiations of elements of high atomic weight have been investigated in detail by Chapman.‡ He finds that the characteristic X-radiation of thorium, in what Barkla has called series L, has a mass absorption coefficient in aluminium of 8·0. This is so far the only characteristic radiation which has been found for thorium. Now since the atomic weight of thorium is 232·5, and that of ionium is 230, the characteristic X-radiations of these elements will probably differ so little in penetrating power that it would be difficult to distinguish between them. It will be noticed that this characteristic X-radiation of thorium has approximately the same value of μ/D as the medium type of γ-radiation (II) found for ionium. It is therefore natural to suppose that all three types of γ-radiation are characteristic radiations, either of thorium or of ionium, of different series. Types I and III belong to no series of characteristic X-rays at present known. It is probable that type III belongs to a series intermediate between series K and L, while type I belongs to a series M or N in Barkla's§ nomenclature. It is of interest to

* Gray, 'Roy. Soc. Proc.,' A, vol. 87, p. 489.

† Rutherford, 'Phil. Mag.,' 1912, vol. 24, p. 453.

‡ Chapman, 'Roy. Soc. Proc.,' A, vol. 86, p. 439.

§ Barkla, 'Phil. Mag.,' 1911, vol. 22, p. 396.

note that, from Rutherford's theory of the constitution of the atom and the mode of production of the γ-rays, it is to be expected that characteristic radiations of several different series are capable of being produced in the atom by suitable agencies. The number of different types of radiation and their relative intensities would vary with the nature of the exciting agency and with the structure of the atom.

The question whether these γ-radiations are excited in the ionium atom itself, or in the surrounding atoms of thorium, is at present quite an open one. One would naturally suppose that, whatever the mechanism of excitation may be, the chance of producing a γ-ray would be much greater inside the atom emitting the α-ray than in any other atom. If, however, a large part of the radiation is excited in the thorium atom, it is to be expected that some radiation would be excited in the platinum upon which the active material is placed. To test this point the active material was transferred to a paper dish equal in area to the platinum dish, and the intensity of the radiation measured for different thicknesses of aluminium. No certain difference in the radiation could be detected. This result does not prove that no radiation was excited in the platinum, for, taking Chapman's value of $\mu/D = 22 \cdot 5$ for the characteristic X-radiation of platinum, it was calculated that 85 per cent. of the radiation would be absorbed in the active material before it reached the electroscope. This important point can be settled by making experiments with the source of α-rays exciting the γ-rays in the form of a very thin film. We hope to do this by depositing a thin film of polonium on different metals, and determining the quality of the γ-radiation in each case.

The γ-Rays from Radiothorium.

A quantity of thorium oxide containing radiothorium equivalent in γ-ray activity to 0·2 mgrm. radium bromide was purified from all β- and γ-ray products by the following method.

The oxide was obtained in solution by the same methods used for ionium. The active thorium hydroxide was completely freed from thorium X by repeated precipitations with ammonia. It was then dissolved in hydrochloric acid, and to this solution was added some lead nitrate and some bismuth nitrate. No precipitate was allowed to form in this solution. The lead and bismuth were precipitated as sulphides by H_2S. The sulphides contained all the thorium B and thorium C. The filtrate containing the radiothorium was evaporated on a water bath till all H_2S fumes were driven off. The solution was acidified, some lead and bismuth salt in solution added to it, and H_2S again passed through it. This operation removes the last

traces of thorium B and thorium C from the radiothorium. To the filtrate was added ammonia in excess, and the precipitated thorium and radiothorium were filtered off as quickly as possible, and ignited. It was immediately placed in a small crystallising dish, which was covered with a thin sheet of mica to make it airtight. The ionisations due to β-rays alone, and to γ-rays alone, were obtained by measuring the activity first with the magnet off, and, secondly, when a magnetic field of about 1500 gauss was applied. This ratio of β-ray to γ-ray intensity of the preparation was measured carefully at frequent intervals for the first five hours, and then at longer intervals for several days.

Immediately after preparation, the leak due to the β-rays from the equivalent of 0·2 mgrm. radium bromide was 1·9 divisions per minute, and that due to the γ-rays alone was 0·5 division per minute. The ratio β/γ is therefore 3·8. Three hours later this ratio was 14·2. After five hours it had become 25·6, the value of the β-radiation now being 17·9, and of the γ-radiation 0·7 division per minute. After 17 hours the ratio was 37·3, the β-radiation now being 140 divisions per minute. After this time the ratio varied little with time. Sixty-seven hours after preparation the leak due to the γ-rays alone was 21 divisions per minute. The rapid growth of β- and γ-radiation is due, of course, to the thorium B, C, and D, formed by the thorium X grown from the radiothorium. The fact that the β- to γ-ray ratio varies so considerably for the first day after preparation, shows that there is some body present initially which emits a much greater proportion of γ-rays to β-rays than the products grown from the radiothorium. This body must be radiothorium. If this body emitted α-rays only, the ratio of β- to γ-rays would be constant with time, no matter how much thorium X and subsequent products were present with it after partial purification. Some weeks later the radiothorium was again purified as carefully as possible, and again a small amount of γ-radiation was found to be "non-separable" from it.

The amount of γ-radiation emitted by radiothorium is of the same order as that emitted by ionium when preparations of equal α-ray activity are measured under the same conditions. No absorption measurements of this γ-radiation have been undertaken, partly on account of the small amount of it, and partly because of the rapid formation of products expelling intense β- and γ-radiation. It is at present difficult to say whether the small β-radiation emitted by radiothorium is due to that body, or to a product grown in the time which elapses between the last precipitation and the first measurement.

It is plain that the discovery of the excitation of γ-rays by α-rays has

opened up a new and interesting field of work, the results of which should have an important bearing, not only on the theory of the nature of the γ-rays and their mode of excitation in atoms, but also on the theory of the constitution of the atom. We are continuing this work by studying in detail the γ- and β-radiations emitted by polonium, radium, and other α-ray products.

Summary.

(1) The work on the excitation of γ-rays by α-rays has been extended to ionium. It is shown that the α-rays of ionium excite γ-radiation, and the nature of this excited γ-radiation has been studied in detail. There is also some slight evidence of the excitation of β-rays.

(2) The γ-radiation from ionium consists of three types. The first of these has a value of μ/D in aluminium of $400\,(\text{cm.})^{-1}$, the second of $8{\cdot}35\,(\text{cm.})^{-1}$, and the third of $0{\cdot}15\,(\text{cm.})^{-1}$. The energy of the radiation is mainly confined to the softest type.

(3) It is probable that these three radiations are characteristic radiations, either of thorium or of ionium, of different series.

(4) Radiothorium emits also a small quantity of γ-radiation, too small, however, to be studied in detail with the quantity of active material at our disposal.

We wish here to express our great indebtedness to Prof. Rutherford, not only for the valuable preparations he has placed at our disposal, but also for his stimulating interest and advice throughout the whole course of the work.

Re-reduction of Dover Tidal Observations, 1883–84, *etc.*

By Edward Roberts, I.S.O., F.R.A.S.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received February 11,—Read February 27, 1913.)

In the 'Proceedings of the Royal Society,' vol. 45, is contained a "Second Series of Results of the Harmonic Analysis of Tidal Observations," collected by G. H. Darwin, LL.D., F.R.S.

In Table I, p. 567, of this paper are included the harmonic constants obtained from the reduction of tidal observations at Dover for the three years 1883, 1884, and 1885. This tidal record was frequently interrupted, and there are wanting 34 days in 1883, 57 days in 1884 and 72 days in 1885. The gaps are generally of short duration, except in 1885, where there is no record from September 24 to October 26. The results generally show far more divergence than is usual, and in consequence many of the smaller tides have been altogether rejected and many of those retained are really bad.

In 1911 there was available a further record of observations, from which a period of one year commencing from 1910, October 1, was selected and reduced by me for the Hydrographic Department of the Admiralty. A comparison of these new results with those contained in the above paper showed a very strong probability that if the gaps in the observations of 1883–85 could be filled in and the observations re-reduced, a much better agreement would be obtained between the results of the three years. On my representation to Sir George Darwin he fully agreed to the desirability of the re-reduction, stating that at the time he had not realised the necessity of filling in the gaps even with rough approximations if the ultimate results were to be fairly reliable. Accordingly Sir George made application and obtained a small grant from the Royal Society fund for the necessary work and obtained for me the original calculations for revision.

On examination of the records it would appear that, in addition to the gaps in 1885, at least, there was evidence of some displacement in time of the actual observations, judging from the value found for the phase of the chief lunar semidiurnal tide (M_2). The value (344°) would make the chief tide about 30 minutes later than those found for 1883 and 1884, a wholly incredible amount. From a close scrutiny of the observations an error appeared probable about 1885, April 16. On this day the last four hourly readings are wanting, and the readings begin again at noon of April 17. The sequence of the heights, however, would indicate that the previous

readings should end, at least, not later than 19h. of April 14. As the rectification of this displacement would entail virtually a re-reduction of the whole year, coupled also with the uncertainty of the correction, it was decided to confine the work to the years 1883 and 1884.

Accordingly, with the newly-found constants, the whole of the curves for the two years were run off on my latest designed machine for tidal predictions, and the heights for the missing days filled in with the values on the machine curves. The whole of the summations were then corrected and the resulting series re-analysed.

For the sake of comparison the results found from the 1910–11 observations are appended.

The values are now as follow:—

Harmonic Tidal Constants at Dover (Long. 1° 19′ E.).

Year beginning	1883. January 1.		1884. January 1.		Mean of 1883–1884.		1910. October 1.	
	deg.	ft.	deg.	ft.	deg.	ft.	deg.	ft.
A_0	=	9·163	=	9·112	=	9·138	=	8·337
S_1	H = / κ = 244	0·030	H = / κ = 285	0·013	H = / κ = 264	0·022	H = / κ = 328	0·020
S_2	H = / κ = 20·5	2·357	H = / κ = 21·9	2·297	H = / κ = 21·2	2·327	H = / κ = 21·4	2·326
S_4	H = / κ = 332	0·047	H = / κ = 18	0·068	H = / κ = 355	0·057	H = / κ = 349	0·058
T	H = / κ = ...	...	H = / κ = ...	...	H = / κ = 33	0·317	H = / κ = ...	...
M_1	H = / κ = 187	0·013	H = / κ = 17	0·019	H = / κ = 77	0·016	H = / κ = 111	0·014
M_2	H = / κ = 329·0	7·553	H = / κ = 329·0	7·445	H = / κ = 329·0	7·449	H = / κ = 331·5	7·085
M_3	H = / κ = 24	0·041	H = / κ = 27	0·036	H = / κ = 25	0·039	H = / κ = 337	0·018
M_4	H = / κ = 215	0·840	H = / κ = 219	0·827	H = / κ = 217	0·834	H = / κ = 222	0·720
M_6	H = / κ = 90	0·211	H = / κ = 93	0·190	H = / κ = 91	0·200	H = / κ = 95	0·153
M_8	H = / κ = 0	0·079	H = / κ = 1	0·069	H = / κ = 1	0·074	H = / κ = 351	0·040
K_1	H = / κ = 48	0·145	H = / κ = 31	0·118	H = / κ = 39	0·132	H = / κ = 39	0·154
K_2	H = / κ = 24·5	0·607	H = / κ = 14·2	0·682	H = / κ = 19·4	0·645	H = / κ = 23·0	0·704
O	H = / κ = 182	0·190	H = / κ = 163	0·177	H = / κ = 172	0·184	H = / κ = 180	0·325
P	H = / κ = 17	0·065	H = / κ = 37	0·045	H = / κ = 27	0·055	H = / κ = 55	0·058

Note.—The values of mean sea-level (A_0) are referred to the zero of the tide-gauge, which is said to be 8·67 feet below the Ordnance datum. The phases of the tides are referred to Greenwich time throughout.

Harmonic Tidal Constants at Dover (Long. 1° 19′ E.)—*continued.*

Year beginning	1883. January 1.		1884. January 1.		Mean of 1883–1884.		1910. October 1.	
	deg.	ft.	deg.	ft.	deg.	ft.	deg.	ft.
J	H = ; κ = 182	0·014	H = ; κ = 231	0·027	H = ; κ = 207	0·021	H = ; κ = ...	...
Q	H = ; κ = 106	0·047	H = ; κ = 99	0·032	H = ; κ = 102	0·040	H = ; κ = ...	...
L	H = ; κ = 330	0·441	H = ; κ = 331	0·455	H = ; κ = 331	0·448	H = ; κ = 328	0·585
N	H = ; κ = 308·4	1·418	H = ; κ = 309·0	1·392	H = ; κ = 308·7	1·405	H = ; κ = 313·9	1·392
2N	H = ; κ = 252	0·083	H = ; κ = 265	0·179	H = ; κ = 258	0·131	H = ; κ = 313	0·299
ν	H = ; κ = 293	0·494	H = ; κ = 272	0·241	H = ; κ = 282	0·368	H = ; κ = 343	0·521
μ	H = ; κ = 45	0·210	H = ; κ = 45	0·269	H = ; κ = 45	0·239	H = ; κ = 41	0·420
2SM	H = ; κ = 231	0·125	H = ; κ = 200	0·113	H = ; κ = 215	0·119	H = ; κ = 216	0·119
MS	H = ; κ = 270	0·528	H = ; κ = 275	0·537	H = ; κ = 273	0·533	H = ; κ = 285	0·732
MN	H = ; κ = 196	0·282	H = ; κ = 197	0·316	H = ; κ = 197	0·299	H = ; κ = 160	0·230
$2M_2K_1$	H = ; κ = 125	0·014	H = ; κ = 50	0·020	H = ; κ = 88	0·017	H = ; κ = ...	...
M_2K_1	H = ; κ = 308	0·087	H = ; κ = 4	0·102	H = ; κ = 336	0·095	H = ; κ = ...	...
M*m*	H = ; κ = 270	0·056	H = ; κ = 226	0·174	H = ; κ = 248	0·115	H = ; κ = 267	0·177
M*f*	H = ; κ = 134	0·112	H = ; κ = 261	0·231	H = ; κ = 198	0·172	H = ; κ = 163	0·062
MS*f*	H = ; κ = 171	0·057	H = ; κ = 336	0·073	H = ; κ = 254	0·065	H = ; κ = 330	0·130
S*a*	H = ; κ = 213	0·978	H = ; κ = 326	0·570	H = ; κ = 270	0·774	H = ; κ = 272	0·283
S*sa*	H = ; κ = 161	0·460	H = ; κ = 192	0·528	H = ; κ = 177	0·494	H = ; κ = 328	0·097

It will be seen that the agreement throughout is now very good and all the tides originally rejected can now be retained as fairly accurate.

The long-period tides have been re-determined, but the very irregular character of the tides at Dover precludes the assumption of their reliability. The mean value, however, of the phase of the solar annual tide accords with the new value of 1910–11, and may be accepted as approximately correct. It also agrees with the phases found for British ports generally.

In connection with this irregularity the following mean daily levels of the water above the zero of the tide-gauge may be noted. The day is the astronomical day commencing at noon :—

1884.	ft.	1884.	ft.	1884.	ft.
September 5......	12·22	September 17......	6·38	September 29......	7·17
" 6......	9·88	" 18......	6·04	" 30......	6·31
" 7......	8·56	" 19......	5·85	October 1......	7·20
" 8......	7·90	" 20......	6·12	" 2......	6·28
" 9......	7·04	" 21......	6·63	" 3......	7·28
" 10......	6·98	" 22......	6·91	" 4......	6·16
" 11......	7·08	" 23......	6·54	" 5......	8·12
" 12......	7·09	" 24......	6·49	" 6......	8·44
" 13......	7·32	" 25......	6·63	" 7......	8·66
" 14......	7·27	" 26......	7·06	" 8......	9·20
" 15......	7·09	" 27......	6·96	" 9......	9·63
" 16......	6·77	" 28......	6·74	" 10......	10·40

The mean level of the water determined for 1884 is 9·11 feet above the tide-gauge zero. The above table shows an excess of over 3 feet on September 5 and a defect of about the same amount on September 19, or a difference of mean level of over 6 feet within a period of 14 days, and for the whole period the mean level of the water is much below the average and only in excess of it on the first two and last three days. The weather conditions during the period are normal and on only one day, September 7, is the atmospheric pressure about three-tenths of an inch below the average with a strong W.S.W. gale, with a wind pressure of over 16 lbs. on the square foot. The average for this day is 8·56 feet, or actually below the yearly average by 0·55 foot, when it would be anticipated to be considerably above it. From this and other considerations it appears probable the heights have been measured from a base 2 feet too high from about September 6 to October 4. The effect of these misreadings on the results will be very little except for the long-period tides, for which it may account in some measure for the divergence of the results obtained for 1883 and 1884.

Studies of the Processes Operative in Solutions. XXV.—The Influence of Non-Electrolytes on Solubility. The Nature of the Processes of Dissolution and Precipitation.

By H. E. Armstrong, F.R.S., and J. Vargas Eyre, Ph.D.

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The subject of "competitive solubility" has been dealt with in two previous communications of this series, Parts II and XI.* In both of these, emphasis was laid on the fact that electrolytes and non-electrolytes are alike active as precipitants of salts from aqueous solutions and it was implied that no "theory" of the process of dissolution which does not take this fact into account can be satisfactory.

The activity of the several precipitants studied was expressed in terms of their apparent molecular hydration—that is to say, the method of treatment adopted involved the evaluation of the amount of water thrown out of action as solvent water by the precipitant: care was taken, however, to point out that this artifice was introduced merely on the ground of convenience and that the expression "apparent molecular hydration" was not to be interpreted literally.

It was contended, in fact, that the precipitant does not act merely by attracting water to itself but that *the condition of the solvent water* must also, in some way, be changed by the introduction of the precipitant, especially in the case of a neutral substance such as propylic alcohol. This was a novel conception, based on views previously brought under the notice of the Society, in 1906, in a communication on the "Origin of Osmotic Effects" and subsequently in Parts II and VI of these studies. The conception has since been extended to other phenomena in Parts XIII, XIV, XV, XVIII, XIX and XX of these studies and a large body of evidence has been brought forward to show that solute and solvent are in all cases *reciprocally* modified.

The experiments now described were instituted mainly in order to ascertain the effects of non-electrolytes on slightly soluble salts, as the hypothesis introduced by Nernst, in 1889, in explanation of the precipitation of one salt by another, was based more particularly on the results obtained with such salts—the hypothesis, namely, that the solubility of a salt is depressed by the presence of another salt if the two have an ion in common.

According to the view put forward by Nernst, the concentration of the "undissociated" part of a salt in a solution saturated with the salt is constant,

* 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 564; 1910, vol. 84, p. 123.

even in the presence of another salt, at each particular temperature; it is also proportional to the product of the concentrations of the ions of the salt (the *ionic solubility product*). If a second salt be introduced which has an ion in common with the salt with which the solution is saturated, a certain proportion of the common ion will be derived from each salt and to maintain the constancy of the solubility product each salt must be re-formed to a certain extent, so that the salt with which the solution was saturated originally is in part precipitated.

As Stieglitz has pointed out,* the hypothesis is based upon premises which are not valid in the case of salts; moreover, though the results obtained with a few slightly soluble salts may appear to substantiate it, the behaviour of soluble salts is in no way in accordance with such an assumption. To take a case in point, when hydrogen chloride is added to a solution of sodium chloride, the latter is all but entirely displaced from solution. An even more striking case is that observed by Étard,† who has shown that potassium chloride is insoluble in a solution saturated with potassium bromide and iodide. The complete command of the water exercised, in the one case, by hydrogen chloride, in the other, by the two haloids is very remarkable.

Peculiarities such as these did not escape the notice of the older workers, as witness the following statements made by Graham in 1850 in his Bakerian lecture on Diffusion :—

"In the consideration of solubility attention is generally engrossed entirely by the quantity of salt dissolved. But it is necessary to apprehend clearly another character of solutions, namely, the degree of force with which the salt is held in solution or the intensity of solvent attraction,‡ quite irrespective of quantity dissolved.

"In the solutions of two salts which are equally soluble in point of quantity, the intensity of the attraction between the salt and water may be very different.

"Besides being said to be small or great, the solubility of a substance has therefore to be described as weak or strong."

The difficulty of evaluating the exact influence one soluble substance will exercise over another in solution must be very great, owing to the existence of peculiarities such as are referred to by Graham. Indeed, to repeat a statement made in Part II, "It can scarcely be doubted that the forces at work in solutions are too complex in character to be expressed as simple mathematical laws. The fact that water is itself a complex material, which varies greatly in composition as the conditions are changed, has been left almost wholly, if not entirely, out of account in discussing electrolytic and

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* 'Journ. Amer. Chem. Soc.,' 1908, vol. 30, p. 946.

† 'Ann. Chim. Phys.,' 1894, (7), vol. 3, p. 275.

‡ This conception is embodied in the term *Haftdruck*, proposed by Traube.

hydration phenomena; and far too little attention has been paid also to the existence of salts in solution in various states of molecular aggregation."

If it be granted that solvent and solute are reciprocally active in the process of dissolution and that the dissolved substance in an aqueous solution is associated with "water," it follows of necessity that when a solution saturated with a particular salt is mixed with a second soluble salt which, *ex hypothesi*, is also hydrated in solution—the second salt being of such nature that no interaction of the two can take place—some of the salt with which the solution was originally saturated must be precipitated, unless the affinity of this salt for water be so strong that it cannot be overcome by that of the added second salt, as in the case observed by Étard: precipitation must continue up to the point at which the two salts share the solvent in certain characteristic proportions.

But any neutral soluble substance which either combines with water on dissolving or in any other way exercises a dehydrating effect (*cp.* § 9) should act in this manner when introduced into the solution and therefore should cause precipitation.

On account of the importance attached by Nernst and others to the behaviour of slightly soluble salts, we have thought it desirable to extend our experiments to the two slightly soluble salts lead chloride and silver acetate and to determine the influence of a number of neutral precipitants not previously studied at the time when the experiments were instituted, though in the interval several accounts have been published by other workers who have had the same problem under consideration. It may be added that the work now recorded was completed in the spring of 1911.

The determinations were all made at 25° C. The substances used were prepared from materials sold as pure (*cp.* XI, p. 124). It was not found possible to estimate with certainty the small quantities of lead chloride present in the solutions by gravimetric methods nor was it possible to effect the determination by the usual volumetric method of titration with a solution of silver nitrate in the presence of potassium chromate as indicator, as a precipitate of silver chromate was formed at once; but by modifying this method, so that all the lead was precipitated as chromate and a slight excess of potassium chromate left to serve as indicator, it was possible to estimate the chloride in the solution by gradually adding a solution of silver nitrate in the ordinary way. If the titration be carried out in a white porcelain basin, satisfactory results are obtained without difficulty. This was established by careful experiments with saturated solutions of lead chloride; the results obtained differed among themselves by less than 1 per cent.

When hydrogen chloride was used as precipitant, the amount of acid present in the pipetted portion of the saturated solution was first determined by titration against standardised alkali; the total chloride present was then determined in the neutral solution by titration with a standardised solution of silver nitrate and the amount of lead chloride present deduced from the two values.

The method used in estimating the amount of silver acetate in the saturated solutions was that known as Pisani's method, which is based upon the fact that an aqueous solution of iodised starch is decolourised by solutions of silver salts. A suitable solution for the purpose was prepared by adding to half a litre of hot water from 10 to 12 grm. of soluble starch made into a paste with water; after boiling the liquid during a few minutes, it was diluted to about 1 litre and mixed with a few drops of an alcoholic solution of iodine, so as to render it a deep blue colour. As it is necessary to use only very dilute solutions of silver salt, the samples of saturated solution were always diluted to 500 c.c.; the diluted solution was titrated against 500 c.c. of the iodised starch solution after this had been standardised against a solution of silver nitrate of suitable strength. With practice, very satisfactory results can be obtained by this method.

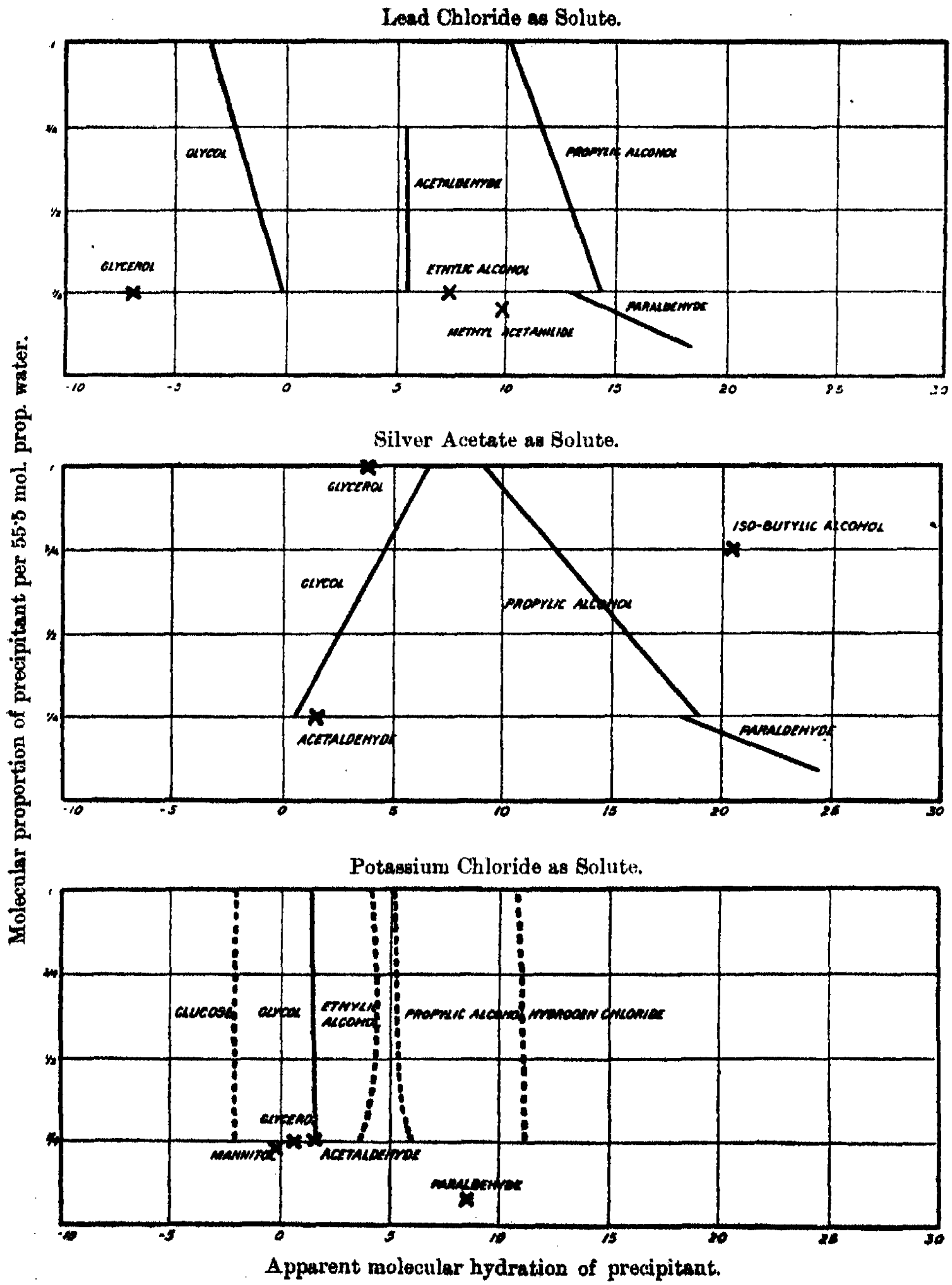
The extent to which the determinations are in agreement is shown in the following table. The results of separate experiments with different samples of salt are given in sections I and II, whilst A and B represent those obtained with two samples of the same solution, the difference being that B was withdrawn an hour later than A:—

100 grms. of water at 25° C. dissolve					
Lead chloride.			Silver acetate.		
		grms.			grms.
I	A	1·1024	I	A	1·096
	B	1·1030		B	1·104
II	A	1·1026	II	A	1·114
	B	1·1021		B	1·117

The results are recorded in the table on p. 238 and are also represented graphically in the diagrams on p. 239.

The effects on the solubility of potassium chloride of a variety of precipitants not previously studied are also recorded in the table and in the graphs.

Precipitant.	Molecular concentration of precipitant per 55·5 mols. of water.	Solubility in 1000 grm. of water at 25°.	Relative density, $d\frac{25°}{25}$.	Molecular solubility.	Apparent molecular hydration of precipitant.
		Lead Chloride.			
—	—	11·0276	1·0098	0·0397	—
Ethylic alcohol	¼	10·6609	1·0069	0·0383	7·39
Glycol	¼	11·0352	1·0116	0·0397	− 0·15
,,	1	11·7035	1·0170	0·0421	− 3·41
Acetaldehyde	¼	10·7638	1·0097	0·0387	+ 5·31
,,	¾	10·2451	1·0095	0·0368	5·25
Paraldehyde	¼	10·8910	1·0114	0·0313	12·83
—	—	11·0210	1·0098	0·0396	—
Paraldehyde	1/12	10·7185	1·0101	0·0385	18·28
Glycerol	¼	11·3658	1·0152	0·0409	− 6·95
—	—	11·0321	1·0104	0·0397	—
Propylic alcohol	¼	10·3266	1·0066	0·0371	14·20
,,	1	10·0262	0·9984	0·0324	10·09
Hydrogen chloride	¼	4·2849	1·0058	0·0154	135·85
,,	½	3·6883	1·0098	0·0132	78·97
Methylic acetanilide	⅛	10·6567	1·0111	0·0383	9·85
Lead nitrate	¼	14·2079	1·0816	0·0510	−63·91
,,	1/10	11·6515	1·0383	0·0420	−31·17
,,	1/50	10·7144	1·0170	0·0386	+79·92
,,	1/100	11·1192	1·0118	0·0400	−43·82
		Silver Acetate.			
—	—	10·2350	1·0081	0·0613	—
Glycol	1	9·0145	1·0154	0·0540	6·62
Glycerol	1	9·5420	1·0277	0·0572	3·76
Propylic alcohol	1	8·5795	0·9981	0·0514	8·98
Paraldehyde	1/12	9·1015	1·0084	0·0535	24·59
—	—	11·1780	1·0085	0·0669	—
Isobutylic alcohol	¾	8·1080	0·9996	0·0486	20·33
Propylic alcohol	¼	10·1335	1·0059	0·0607	18·75
Glycol	¼	11·1570	1·0099	0·0668	0·42
—	—	10·4250	—	0·0625	—
Acetaldehyde	¼	10·3361	—	0·0619	1·45
Paraldehyde	¼	9·5478	—	0·0572	18·20
		Potassium Chloride.			
—	—	367·700	1·1820	4·9315	—
Acetaldehyde	¼	375·119	1·1791	4·8968	1·56
Paraldehyde	1/12	363·051	1·1786	4·8692	1·42
Glycol	¼	365·134	1·1802	4·8970	1·51
,,	1	359·100	1·1762	4·8160	1·30
Glycerol	¼	366·700	1·1830	4·9194	0·56
Mannitol	¼	367·455	1·1903	4·9285	0·15
,,	3/16	368·000	1·1884	4·9360	− 0·22


Lead Chloride as Solute.
GLYCOL
ACETALDEHYDE
PROPYLIC ALCOHOL
GLYCEROL
ETHYLIC ALCOHOL
PARALDEHYDE
METHYL ACETANILIDE
Silver Acetate as Solute.
GLYCEROL
ISO-BUTYLIC ALCOHOL
GLYCOL
PROPYLIC ALCOHOL
ACETALDEHYDE
PARALDEHYDE
Potassium Chloride as Solute.
GLUCOSE
GLYCOL
ETHYLIC ALCOHOL
PROPYLIC ALCOHOL
HYDROGEN CHLORIDE
GLYCEROL
MANNITOL
ACETALDEHYDE
PARALDEHYDE
Molecular proportion of precipitant per 55·5 mol. prop. water.
Apparent molecular hydration of precipitant.

1. Taking into account the observations of other workers as well as those brought forward in this and the two previous communications, it is clear that, in principle, no distinction can be drawn between slightly soluble salts and soluble salts. Owing to the difficulty which attends the determination of solubility in the case of slightly soluble salts, we do not attach weight to the smaller differences observed between the lead and the silver salt, the more as we found it impossible to obtain constant values in the case of the latter, different samples giving different values—whether on account of surface changes due to the action of light or to differences in the state of aggregation (*cp.* XI, p. 125). For example, we are not prepared to regard propylic alcohol and paraldehyde as more active precipitants of the silver than of the lead salt but are inclined to think that the activity of both precipitants, when present in small proportions, may have been over-estimated in the case of the silver salt.

2. Non-electrolytes and electrolytes alike act as precipitants of salts; though in both cases substances are to be found which increase solubility instead of depressing it.

3. As the activity of non-electrolytes as precipitants is inconsistent with the postulates of the ionic hypothesis, it is obvious that the explanation of the behaviour of precipitants in general must be based upon some broader hypothesis.

4. It is necessary, in all cases, to take into account the changes which affect the solvent as well as those that affect the solute; to neglect consideration of the changes in the solute—the almost universal habit of those who postulate the existence of dissociated, separate ions in solutions of electrolytes—is an indefensible practice.

5. If it be admitted that both solids and liquids are formed by the association of the fundamental molecules characteristic of the gaseous state, dissolution must be regarded as in large measure a process of "depolymerisation" not of the solute alone but also of the solvent.

6. It is also necessary, far more than has been customary of late, to take into account the reciprocal changes which attend dissolution, other than those which involve disturbance of molecular complexity, namely, those which involve the formation of new molecular species, whether as the outcome of interactions or of mere association of solvent and solute.

7. One of the most striking facts brought out when the evidence now available is considered, is the remarkable antithesis presented by the activity of electrolytes and non-electrolytes as precipitants: whereas, in aqueous solutions, the former are usually the more active the more soluble they are, in the case of non-electrolytes the relationship is of the reverse order.

8. The simplest case to be considered is that of carbon dioxide; as the molecules of this gas are unlikely to be present in solution in any other form than as simple molecules such as are represented by the formula CO_2, any increase in its solubility cannot well be interpreted otherwise than as due to an increase merely in the number of molecules undergoing some form of hydration which renders them soluble.

Usher's determinations of the solubility of this gas in presence of various organic substances* are, therefore, of particular value. From experiments made with semi-normal solutions, he has deduced the results displayed in the following table, the value given being the number of cubic centimetres of gas dissolved by 1000 grm. of water at 20° in presence of the substance quoted:—

	Water	878	8.	Pyrogallol	894
1.	Cane sugar	797	9.	*n*-Propylic alcohol	902
2.	Mannitol	833	10.	Acetamide	906
3.	Dextrose	841	11.	Urethane	907
4.	Glycine	864	12.	Catechol	908
5.	Carbamide	884	13.	Quinol	928
6.	Thiocarbamide	885	14.	Antipyrine	935
7.	Acetic acid	893	15.	Resorcinol	945

9. In the case of the three substances first on the list, the observed lowering of the solubility cannot well be regarded otherwise than as a direct dehydration effect, that is to say, as due to a diminution in the amount of free water present owing to the association of a certain amount of the water used with the added solute.

Excluding Nos. 4, 5, 6, 10, 11 and 14, which conceivably may exercise an influence as basic compounds, though perhaps scarcely to the extent observed, the remaining substances apparently all serve to render the water *more active as a solvent* of carbon dioxide—more effective, that is to say, in converting it into a "hydrated" form. Now the view advocated in previous communications of this series involves the assumption that when neutral substances are dissolved in water they serve to increase the proportion of simpler molecules in the liquid—*i.e.*, molecules of hydrone, OH_2—and, therefore, to render it a more active agent.

10. Confining our attention to propylic alcohol, the only one of the substances under consideration of which we have experience, which is an active precipitant of salts—more active, in fact, than ethylic alcohol—the increase in the solubility of carbon dioxide in its presence, amounting to 24 c.c., cannot well be ascribed to the direct dissolution of the gas in the alcohol.

* 'Chem. Soc. Trans.,' 1910, p. 66.

Ethylic alcohol depresses the solubility of carbon dioxide in water. The coefficients found by Findlay and Shen* are as follows (at 25°, 737–747 mm.):—

Water				0·825
„ containing	2·95 grm. alcohol	(in 100 c.c.)	......	0·812
„ „	3·01 „	„	......	0·814
„ „	8·83 „	„	......	0·786

As ethylic alcohol undoubtedly has a greater affinity for water than propylic, it may be supposed that it is far more completely hydrated and more under the control of the water than is propylic alcohol: consequently, that more molecules of the latter alcohol may be active in promoting dissociation of water molecules in the sense of the expression $(OH_2)_x \rightarrow xOH_2$.

On this assumption, a larger proportion of the molecules of carbon dioxide would be subject to hydration in a solution of propylic than in one of ethylic alcohol: hence the increase in solubility. The argument is of general application.

11. When the results we have obtained with silver acetate, lead chloride and various haloids and those obtained by Rothmund† with silver sulphate, potassium bromate, potassium perchlorate and lithium carbonate—four sparingly soluble salts which are more soluble than the two we used but less soluble than the remainder of those we have studied—are contrasted, the same substances are seen to act as precipitants and, with certain marked exceptions, the order of their activity is the same.

12. In cases in which direct comparison is possible, *the less* soluble non-electrolyte is always the more active precipitant: thus the activity of the monhydric alcohols is in the order of increasing molecular weight. Paracetaldehyde is more active than acetaldehyde, whether comparison be made of equal weights or of molecularly similar proportions. The activity of polyhydric alcohols diminishes as their hydricity and solubility increases. Thiourea is more active than urea.

13. The experiments carried out by Fox and Gauge on the solubility of potassium sulphate‡ and by Rothmund on the salts above mentioned are of special interest in this connexion.

The solubility of potassium sulphate is at first unaffected by the presence of cane sugar and is only slightly diminished as the proportion of sugar is increased; obviously, therefore, as it must be supposed that cane sugar

* 'Chem. Soc. Trans.,' 1911, p. 1313.

† 'Zeit. phys. Chem.,' 1909, vol. 69, p. 523.

‡ 'Chem. Soc. Trans.,' 1910, p. 377.

becomes associated with a certain proportion of the water, it must serve from the beginning to promote the solubility of the salt. Mannitol, glycerol, glycol, pyridine, ethylic alcohol and acetone are active as precipitants from the beginning, in the order mentioned.

Most unfortunately, Rothmund's experiments were carried out with *volume* normal solutions: consequently, no two solutions contained the same molecular proportion of precipitant and water, so that the results are not comparable among themselves. Nevertheless, it is obvious, when strictly neutral precipitants such as the monhydric alcohols are considered, that these maintain their position in order of activity whatever the salt used may be.

The cases in which the precipitants vary in behaviour are significant. Thus, whilst glucose promotes the dissolution of silver sulphate and of lithium carbonate, it hinders that of potassium bromate. Similar differences are observed in the case of cane sugar. Obviously therefore the behaviour of the salts of the "dibasic" acids is different from that of the monobasic: both sulphuric and carbonic acids, however, appear to be in reality monobasic acids upon which a slight extra activity is imposed; it may well be that an exchange of radicles takes place between such salts and basic substances such as the sugars.

On the other hand, whilst phenol increases the solubility of silver sulphate, it depresses that of potassium bromate and perchlorate—but acetic acid acts as a weak depressant in all cases.

It is significant also, from this point of view that acetonitrile promotes the solubility of silver sulphate whilst acting as a precipitant of lithium carbonate: it is well known that nitrogen compounds have a specially strong affinity for silver salts.

Similar interpretations may be given of other cases of "irregularity."

14. Propylic alcohol, which promotes the solubility of carbon dioxide, is a powerful precipitant of salts. The assumption made previously (§ 8), it may be pointed out here, is a satisfactory explanation of this difference. In the case of carbon dioxide, an increase of solubility may be explained as the consequence of an increase of the active agent in the solution, that is to say in the number of molecules of hydrone, OH_2.

In the case of salts, however, though an increase in the proportion of molecules of hydrone would render the liquid a better solvent of the salt, it would also favour the tendency of the fundamental molecules of the salt to combine among themselves, as action would set in between hydrone molecules in the solution and those attached to the salt; in other words, an increase in the number of hydrone molecules would render the solution a dehydrating medium.

15. In the case of salts, an additional force is operative which cannot come into existence in a case such as that of carbon dioxide. In the solid state, all salts presumably are "polymerised" forms of their fundamental molecules and on entering into solution, such molecules are more or less, if not entirely, dissociated. The solubility of a salt may be said, in fact, to be determined by the two sets of affinities pictured in the expressions

$$(RX)_n \rightleftharpoons nRX$$
$$x(RX) + y(OH_2) \rightleftharpoons (RX)_x(OH_2)_y,$$

the solubility in each particular case depending on the extent to which the two opposite tendencies come into play. Both forms of dissociative change shown in the equations would be promoted by those precipitants especially which have but slight affinity for water, as such molecules would be most effective mechanically.

The difference between salts generally and the corresponding acids is probably due to the fact that the acid radicle is more effectively held in check or neutralised by hydrogen than by any metal; and the differences in salts may be attributed to the different extents to which the metals "saturate" the acid radicles. On such a hypothesis, it is possible to understand that a metal should have the relatively constant effect which it is known to have in salts.

In the case of a very difficultly soluble salt such as is silver chloride, the affinity of the individual fundamental molecules for one another appears to be very great. It is not improbable that in so far as such a salt is soluble at all, it enters into solution only in its simplest form represented by the symbol AgCl. This molecule may be very active; it may be so fully activated, in fact, as to be completely "dissociated"—to use the now conventional term. The solubility of the salt is slight because the affinity between the fundamental molecules is so special that it prevails almost entirely over the affinity which hydrone has for these molecules. In the case of soluble salts the balance is far more nearly even. The fact that salts generally are not precipitable by neutral substances in the inverse order of their solubility is probably to be explained by considerations of this order.

16. It will be noticed that in the case of lead chloride and silver acetate the graphs of propylic alcohol and paraldehyde slope backwards—in other words these substances are the more active as precipitants the smaller the proportion present. In all probability, as the amount present is increased, they tend more and more to promote the dissociation of the complex molecules of the salts into simpler more soluble molecules.

17. There can be little doubt that the polyhydric alcohols and sugars especially act mainly when not entirely as direct dehydrating agents.

In cases in which solubility is increased by such substances there can be little doubt that this is because more soluble substances are formed by the interaction of the substances present. It is well known that the sugars form compounds with salts.*

18. In all cases, a soluble substance must exercise some influence directly as a dehydrating agent; but the influence it exercises in this way must diminish and the effect it has on the solvent must increase as the solubility of the substance diminishes; in so far, however, as the added substance induces the dissociation of complex molecules of the solute, its action will be to increase solubility.

19. In fine, complex as the phenomena with which we have to deal in aqueous solutions undoubtedly are, it appears to be possible to interpret them on broad and general grounds by the application of ordinary chemical principles. Little more is required than to extend to oxygen the conceptions which are accepted in the case of carbon.

20. It is only necessary to assume that water is a complex material consisting of a variety of molecular species in proportions which vary with the temperature, some comparable with the polymethylenes, others with hydrols (*cp.* Parts VI, XIX, XXIV).

Further, to assume that when substances are dissolved in water they are hydrolated and hydronated in various ways and to various extents and at the same time produce variations in the water (XVIII).

Lastly, to admit that the several forms of "hydrated" compound are not all active chemically and that those which are active are not all equally so—as in the case of the polymethylenes.

Such assumptions made, it follows that every variation in the conditions will involve variation not only in the active but also in the inactive constituents of the solution; in other words, both components of a solution must vary as the conditions are varied.

[The authors are indebted to Mr. F. W. Jackson for the assistance which he has given them in carrying out their experiments.]

* The greater solubility of lead chloride in presence of lead nitrate cannot well be accounted for otherwise than as the consequence of the formation of a mixed salt, $PbCl(NO_3)$.

Studies of the Processes Operative in Solutions. XXVI.—*The Disturbance of the Equilibrium in Solutions of Fructose by Salts and by Non-electrolytes.*

By E. E. WALKER, B.Sc.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received January 1,—Read February 13, 1913.)

One of the main objects in view throughout these studies has been to determine the manner in which non-electrolytes influence the course of change in solutions: it has been shown that they affect the rate at which cane sugar is hydrolysed (XII); also the rate at which urea is formed from ammonic cyanate (XX); and to judge from the behaviour of methylic acetate as a hydrolyte in comparison with that of cane sugar, it is probable that the degree of "hydration" of acids and salts in solution is lowered by their presence (XXIII).

At Prof. Armstrong's request, to throw further light on such phenomena, I have ascertained the effect produced by a variety of non-electrolytes on fructose in aqueous solutions.

The further study of this substance was desirable on various grounds, especially on account of the important part it plays in plant metabolism. It is known to vary in optical activity to a marked extent, the temperature coefficient of an aqueous solution being larger than that observed in the case of any other sugar, viz. $[\alpha]_D = 0^\circ{\cdot}70$ per degree Centigrade. The rotatory power of the sugar in solution is decreased both by heating and by the addition of alcohol but increased by concentration, by salts and by acids; it appeared therefore to be a specially suitable substance to use, as the course of any change could be followed with the polarimeter.

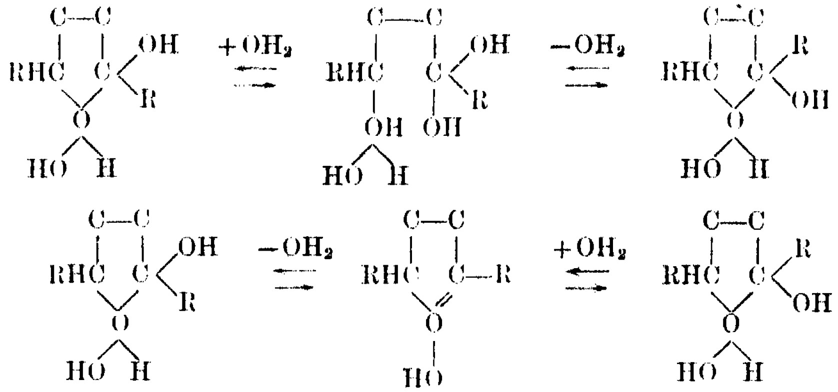
Little is known at present of the behaviour of fructose towards salts in comparison with that of glucose and cane sugar; it was desirable, therefore, that it should be studied from the point of view from which these sugars have been considered (X and XV).

Mr. Worley has drawn attention recently to the alteration in the degree of optical inversion which attends the inversion of solutions of cane sugar of different degrees of concentration (XXII, p. 571) and has pointed out that probably an explanation is to be found in changes in the rotatory power of the fructose in presence of the acid. The further study of fructose appeared to be of importance also in this connexion.

The material used was Kahlbaum's crystalline fructose prepared from inulin. Except when stated otherwise, all measurements were made in

a 400 mm. jacketed tube, the temperature being maintained at $25° \pm 0°·005$. The observations were carried out in mercury green light with the polarimeter and apparatus described in Part XXII.

It is commonly admitted that glucose exists in solution as an equilibrated mixture of the two stereoisomeric forms and it has been supposed that fructose also occurs in corresponding forms.* The change from the one isodynamic form into the other may be pictured as taking place in one or other of two ways ($R = CH_2·OH$) :—



Whether, in the process of interconversion, the intermediate (ketohydrol or ethenoid) compound is ever formed in any considerable proportion must be left an open question at present.

Whilst the oxygen atom in the ring system may be pictured as in the plane of the ring in the one form of fructose, it is to be supposed that in the isomeric form, this oxygen atom is deflected out of the plane of the ring: hence it is, Hudson contends,† that the one form is dextrorotatory, the other lævorotatory. Presumably the two forms of glucose are similarly related: in point of fact, though both forms are dextrorotatory (β-glucose $[\alpha]_D^{20°} = +20°$), the β-glucosides are all lævorotatory compounds, thus :—

β-methyl-glucoside	....	$-32°$
β-ethyl ,,	....	$-33·4°$
β-propyl ,,	....	$-34·9°$
β-butyl ,,	....	$-35·4°$
β-isobutyl ,,	....	$-34·9°$
β-allyl ,,	....	$-40·3°$
β-benzyl ,,	....	$-49·8°$

* Compare E. F. Armstrong's 'The Simple Carbohydrates and the Glucosides,' Longmans and Co.

† 'Amer. Chem. Journ.,' 1909, vol. 31, p. 66.

To avoid periphrasis, it is proposed to speak provisionally of the one form of fructose as *fructodextrose* and of the stereoisomeric compound as *fructolævose* rather than as α- and β-fructose.

Assuming that the active compound in a solution is the "oxonium hydrol," in whatever way they are hydrated, to account for the difference in stability of the two forms, it is almost necessary to suppose that fructolævose forms a more stable "hydrate" than fructodextrose, as the passage from the former into the latter is promoted by heating. The fact established by H. T. Brown and S. U. Pickering that the heat of conversion from the (β) lævo- into the (α) (?) dextro-form is a relatively high negative value may be regarded as strong evidence in favour of this view,* thus:—

Fructose	$\beta \rightarrow \alpha+\beta$	......	-835 calories
Glucose	$\alpha \rightarrow \alpha+\beta$	......	106 ,,
Milk sugar ...	$\alpha \rightarrow \alpha+\beta$	......	34 ,,

According to Hudson, cane sugar is resolved initially into α-glucose and fructodextrose ($[\alpha]_D = +17°$), that is to say, it is derived from corresponding forms of aldose and ketose. Both forms of fructose and glucose undergo "mutarotation" at unimolecular rates, though the change takes place much more rapidly in the case of the former.†

My own observations confirm those made by Hudson that the large temperature coefficient of fructose is due to a change in the proportions in which the two isodynamic forms are in equilibrium at different temperatures. The same constant was obtained by following the course of the mutarotation in a solution which had been quickly prepared as in one which had either been cooled, then suddenly heated to 25° and brought under observation or had been heated and then quickly cooled to 25° before observation (Table I).

Suspecting that the change in rotatory power produced by alcohol is due to a similar cause, a solution of fructose was prepared by dissolving the sugar in the proportion of two molecular proportions to 100 of water; after a couple of hours, the solution was cooled quickly to 22°, then mixed with 35 molecular proportions of ethylic alcohol which had been weighed out separately. The temperature rose almost to 25°; it was quickly adjusted to 25° and the rise in rotatory power followed in the polarimeter.

Subsequently the solution was cooled in the ice chest, then heated rapidly to 25° and observations made as before. The results are given in Table II. The mean constants are practically identical: whence it follows that the change in rotatory power caused by alcohol is due to the same cause as that

* 'Chem. Soc. Journ.,' 1897, p. 756.

† Hudson, 'Amer. Chem. Soc. Journ.,' 1908, p. 1564.

produced by heat. It may be pointed out that the rate of change in presence of alcohol is lower.

Table I.

Mutarotation.				Cooling.			
t (minutes.)	α.	$\alpha - \alpha_x$.	$\frac{1}{t}\log\frac{\alpha_1-\alpha_x}{\alpha_2-\alpha_x}$.	t.	α.	$\alpha - \alpha_x$.	$\frac{1}{t}\log\frac{\alpha_1-\alpha_x}{\alpha_2-\alpha_x}$.
0	112·25	6·06	—	0	110·68	4·49	—
2	110·03	3·34	0·099	$1\frac{1}{2}$	109·41	3·22	·096
4	108·68	2·49	·094	5	107·73	1·54	·092
6	107·82	1·63	·092	7	107·16	·97	·100
8	(107·21)	(1·02)	—	9	106·82	·63	·094
11	106·75	·56	·094	11	106·61	·42	·086
14	106·48	·29	·097	13	106·46	·27	·095
17	106·34	·15	·095	16	106·23	·14	·099
22	106·25	·06		20	106·16	·07	
44	106·19			33	106·19		
86	106·19			80	106·19		
	Mean		0·0951		Mean		0·0946

Table II.

Alcohol.				Cooling.			
t.	α.	$\alpha - \alpha_x$.	$\frac{1}{t}\log\frac{\alpha_1-\alpha_x}{\alpha_2-\alpha_x}$.	t.	α.	$\alpha - \alpha_x$.	$\frac{1}{t}\log\frac{\alpha_1-\alpha_x}{\alpha_2-\alpha_x}$.
0	97·36	6·23	·044	$\frac{1}{2}$	99·25	7·92	
1	96·76	5·63	45	2	98·21	6·88	·041
4	95·24	4·11	435	$3\frac{1}{2}$	97·08	5·75	·052
6	94·50	3·37	46	5	96·33	5·00	·040
8	93·91	2·78	42	7	95·33	4·00	·048
10	93·41	2·28	43	9	(94·80)	(3·47)	—
13	92·83	1·70	425	11	94·01	2·68	·0435
16	92·375	1·245	45	14	93·345	2·015	·042
20	91·93	·80	48	18	92·535	1·305	·0465
24	91·655	·525	46	23	92·095	·765	·0435
32	91·36	·23		30	91·66	·33	
42	91·205	·075		50	91·33*		
62	91·13			120	91·32		
75	91·13						
	Mean		0·0445		Mean		0·0444

* This higher value is probably due to the escape of alcohol, which is liable to be gradually absorbed by the cork closing the aperture in the polarimeter tube.

From experiments in which alcohol was added in various proportions up to that of 50 molecules to 100 of water, the solution containing half a molecular

proportion of fructose, it appears that the change in rotatory power is nearly proportional to the amount of alcohol added.

The results obtained with various substances are collected in Table III. As it has been observed in other cases that the effects produced by non-electrolytes are not quite proportional to the quantity added, the calculated values given in the fifth column are not to be regarded as strictly comparable but rather as indications of the order of activity of the substances.

Table III.

Substance added.	Molecular proportion per 100 mols. water.	$[\alpha]^{25°}_{Hg}$.	Observed change.	Change per molecular proportion.
		°	°	°
Fructose alone	1·00	−105·02		
"	2·00	−106·30	−1·28	−1·28
*Sodium chloride	2·00	−108·77	−3·75	−1·88
*Potassium chloride	2·00	−109·12	−4·10	−2·05
Cane sugar	0·788	−108·26	−1·76	−2·50
Phenol	1·53	−107·17	−0·87	−0·59
Methylic alcohol	8·48	−102·93	+3·37	+0·397
Ethylic alcohol	5·00	−102·06	+4·24	+0·848
Propylic alcohol	5·00	−100·60	+5·70	+1·14
Isobutylic alcohol	1·50	−103·95	+2·35	+1·57
Amylic alcohol (fusel oil)	0·37	−105·62	+0·68	+1·84
Allylic alcohol	5·44	−102·16	+4·14	+0·762
Methylal	1·22	−105·26	+1·04	+0·853
Paraldehyde	0·89	−105·13	+1·17	+1·32

* These solutions contained only one molecular proportion of sugar; the rest contained two.

It will be noticed that the alcohols of the ethylic series, as well as methylal and paraldehyde, appear to have promoted the formation of fructodextrose; phenol, cane sugar, fructose itself and sodium and potassium chlorides, so far as alteration in rotatory power is concerned, appear to have the opposite effect.

The question to be considered is whether the apparently opposite effects produced by the two sets of substances are due to the occurrence of opposite changes in the solutions.

Taking into account observations made in other cases, there is reason to suppose that, as pointed out above, the effect produced by the alcohols is the same as would be produced by heating—that is to say, they exercise a dissociating and "dehydrating" effect; the fact that the activity of the alcohol is greater the higher its molecular weight and the less soluble it is in water is in harmony with this conclusion.

But salts and even cane sugar should also produce a concentrating and dehydrating effect, as they withdraw water from the solution; it might,

therefore, be expected that the proportion of fructodextrose would be increased, not diminished as it appears to be, in their presence.

The mere concentration of the solution will account only for part of the increase in negative rotatory power; but in this connexion, the question arises whether the negative increase which attends concentration should be ascribed to an increase in the proportion of fructolævose present rather than to the formation of an increased proportion of complex molecules of higher negative rotatory power; in any case, it is scarcely probable that the rotatory powers observed are those produced entirely by substances present in the state of simple molecules.

It is reasonable to suppose that, in the case of the salts examined, the change in rotatory power is in part, it may be in large part, due to the formation of compounds of salt with sugar. It is well known that such compounds exist and a large body of evidence in favour of the view that even cane sugar will combine with salts in solution was brought forward in Part X of these studies. The magnitude of the effect produced by potassium chloride in the case of several sugars is as follows, the values given being those observed in solutions containing a single molecular proportion of salt, half a molecular proportion of sugar and 50 of water:—

Fructose	4·10°	Lactose	0·17°
Glucose............	1·33	Melibiose	0·31
Cane sugar	0·96	Raffinose	0·04

It will be observed that the value is relatively high, not only in the case of fructose but also in that of cane sugar—which itself contains a fructose residue, though not one derived from fructolævose.

Taking into account the observations recorded in Part XV that β-methylglucoside is a more active compound than the isomeric α-compound and that in presence of salts its rotatory power suffers the greater change, it is possible that fructolævose would be the more active and the more likely to combine with salts. It therefore appears not improbable that the dehydrating tendency of the salt may be overcome by the tendency of the salt to combine with the fructose and that in consequence the salt may determine the formation of a larger proportion of fructolævose.

Acids may be supposed to act similarly; moreover, the peculiar behaviour of the acid-alcohol, phenol, lends support to such a view. It was to be expected that this compound would behave like one of the less soluble alcohols of the ethylic series; such is not the case, however.

It is only logical to extend the explanation here advanced to cane sugar; it should be mentioned that the value arrived at in the case of this sugar is

based on the assumption that it retains its own specific rotatory power in presence of fructose. If it be granted that the increase in the rotatory power of fructose on concentration is due to the formation of an increased number of polymerised molecules, it must be admitted to be possible that molecules of fructose can combine with the fructose section in cane sugar and that in this case also fructolævose may be the more active substance.

It is hoped that it may be possible to throw further light on the problem and to test the explanation now offered provisionally by extending these observations and particularly by studying the behaviour of the methyl-fructosides in comparison with that of fructose.

[It is obvious that if so delicate a difference as that which distinguishes the two isomeric forms of fructose can determine a difference in their behaviour towards salts—and salts can therefore determine the formation of the one form rather than of the other, we are brought face to face with conditions of special interest on biological grounds. It is to be supposed that the systematic study of such refined cases of chemical change will be of material service in enabling us gradually to interpret mysteries presented by vital phenomena. The influence of potassium salts in particular on the formation of carbohydrates in plants and the special value of such salts in promoting animal metabolism are cases in point.—H. E. A.]

Factors Affecting the Measurement of Absorption Bands.

By H. HARTRIDGE, M.A., Fellow of King's College, Cambridge.

(Communicated by Prof. J. N. Langley, F.R.S. Received November 1, 1912,—Read January 16, 1913.)

[This paper is published in Series B, vol. 86 (No. B 585).]

An Apparatus for Liquid Measurement by Drops, and Applications in Counting Bacteria and other Cells, and in Serology, etc.

By R. DONALD, B.Sc. (N.Z.), D.P.H. (Oxf.).

(Communicated by Dr. L. Hill, F.R.S. Received November 21, 1912,—Read January 16, 1913.)

[This paper is published in Series B, vol. 86 (No. B 586).]

The Liberation of Ions and the Oxygen Tension of Tissues during Activity. (Preliminary Communication.)

By H. E. ROAF, M.D., D.Sc.

(Communicated by Prof. C. S. Sherrington, F.R.S. Received January 10,—Read February 20, 1913.)

[This paper is published in Series B, vol. 86 (No. B 586).]

An Investigation into the Magnetic Behaviour of Iron and some other Metals under the Oscillatory Discharge from a Condenser.

By E. W. MARCHANT, D.Sc., M.I.E.E., David Jardine Professor of Electrical Engineering in the University of Liverpool.

(Communicated by Prof. S. P. Thompson, F.R.S. Received December 13, 1912,—Read January 30, 1913.)

Introduction.

1. The principal object of this investigation was the determination of the relation between magnetising force and permeability when iron or nickel is subjected to alternating magnetisation obtained from the oscillatory discharge of a condenser, especially with a view to finding the permeability with large magnetising forces.

A good deal of work has been done on this subject, that which is most akin to that described in this paper has been carried out by Battelli and Magri,* who have observed the phenomenon of the oscillatory discharge with varying period as first described by the author in a letter to 'Nature.'† The highest value of magnetising force employed in their experiments was about 700 C.G.S. units whereas the range covered in the tests herein described was from 500 to 5000 C.G.S. units.

Other workers in the same field have been Hertz,‡ Jouast,§ Schames,‖ Zahn,¶ Varley,** Hemsalech,†† Zenneck,‡‡ Fleming,§§ Birkeland,‖‖ Sir J. J. Thomson,¶¶ C. E. St. John,*** Klemincic,††† Trowbridge,‡‡‡ and Pellat.§§§

* 'Accad. Lincei Atti,' vol. 15, pp. 63–74.
† 'Nature,' vol. 62, p. 413.
‡ 'Wied. Ann.,' vol. 26, p. 427.
§ 'Soc. Int. Elect. Bull.,' 1911, Ser. 3, vol. 1, pp. 49–57.
‖ 'Ann. d. Physik,' vol. 27 (1), pp. 64–82.
¶ 'Deutsch. Phys. Gesell. Verh.,' vol. 11 (8), pp. 185–204; vol. 11 (18), pp. 377–381.
** 'Phil. Mag.' (6), vol. 3, pp. 500–512.
†† 'Comptes Rendus,' vol. 132, pp. 917–920.
‡‡ 'Ann. d. Physik,' vol. 12 (4), pp. 869–874.
§§ 'Roy. Soc. Proc.,' vol. 70, p. 398.
‖‖ 'Comptes Rendus,' June, 1894.
¶¶ 'Recent Researches in Electricity and Magnetism,' p. 302.
*** 'Phil. Mag.' (5), vol. 38, p. 425.
††† 'Wien. Akad. Sitz.,' vol. 107, p. 330.
‡‡‡ 'Ann. d. Physik,' vol. 12 (4), pp. 869–874.
§§§ 'Comptes Rendus,' June 11, 1894.

Method of Observation.

2. The method adopted in this investigation was to photograph the image of the spark produced by the condenser discharge reflected from a revolving mirror (see fig. 1). This method was similar to that originally adopted by

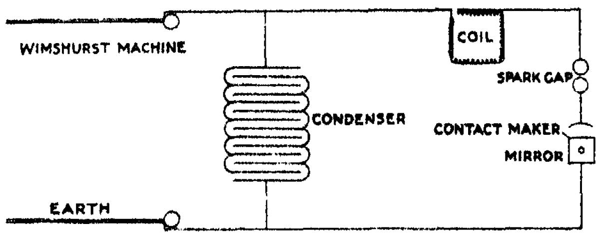


Fig. 1.—Diagram to show arrangement of circuit.

Feddersen and Schiller, but in this case the surface of the mirror was flat and the light from the spark was focussed by a lens on to the photographic plate.

The mirror used in most of the experiments was formed with four silvered glass plates supported in a square aluminium frame, each mirror being 1 inch by 4 inches. This could be run with safety up to 100 revolutions per second. For higher speeds a small silver mirror was used with a reflecting face ½ inch by 2 inches, which was run up to 230 revolutions per second. The speed of the mirror was determined by a contact wheel driven by a worm cut in the shaft of the mirror, the contacts being arranged in one of the circuits of a double chronograph, the second circuit was connected to a clock giving seconds, and the speed could be measured to within ¼ per cent. The spark gap was made with brass balls and its length was measured by a micrometer. The circuit of the spark was closed through a contact-maker formed of a brush of fine wires attached to the frame of the mirror, which rubbed against a brass plate. This contact-maker gave excellent results, chiefly because of the high speed at which the brush was revolved.

Condensers.

3. The condensers used consisted, in the first experiments, of a number of Leyden jars each having approximately 0·004 microfarad capacity. A second small condenser, sometimes used, consisted of nine plates of glass, 2 feet square, on which were pasted sheets of tinfoil 18 inches square, the glass being carefully shellacked and the whole well insulated.

The third condenser (the one chiefly used) consisted of 10 sets of 10 glass plates 3 feet square, coated with tinfoil 2 feet square, the glass being

approximately 0·063 inch thick. The capacity of each set of 10 plates was about 0·14 microfarad, giving a total capacity of nearly 1·4 microfarads, which would stand, if necessary, 30,000 volts. The condenser, however, was never used at so high a voltage, except for test purposes; the normal discharge, as stated above, taking place at about 10,000 volts.

An air condenser was also used consisting of 30 sheets of zinc 18 inches square, placed 0·25 inch distant from each other, and having a capacity = 0·010 microfarad. This latter condenser was not used in the special experiments under consideration, but merely to obtain a result to test how nearly the observed and calculated frequencies agreed for the coils used in the experiments. The capacity of these condensers was compared by a ballistic method with the capacity of a standard Elliott ½-microfarad condenser, which had been calibrated at Glasgow University by comparison with the standards there, and also by testing with the instruments at hand in the laboratory.

Coils.

4. The coil chiefly used was square in shape, made of a single layer of No. 16 guttapercha-covered wire wound on a tube of shellacked paper. The tube was made square, in order to facilitate the introduction of cores of suitable materials. And, by using a single-layer coil, it was possible to get a more accurate approximation to the apparent permeability of the substances introduced than with a coil of several layers, in which the proportion of the area of each layer influenced by the introduction of the coil varied for the

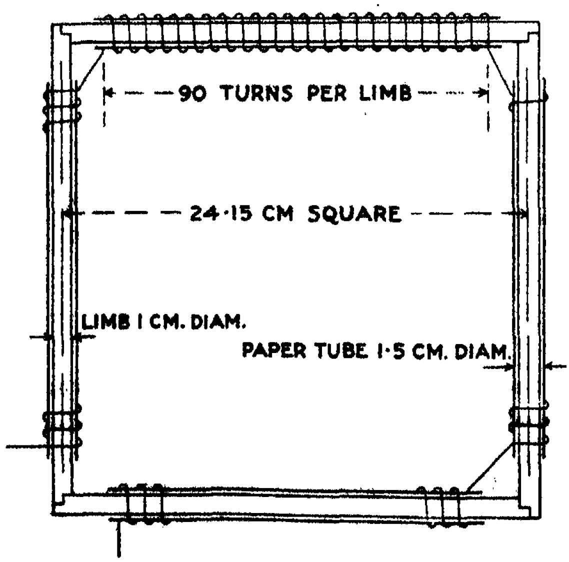


FIG. 2.

different layers. Each side of the square coil contained 90 turns, the diameter of each turn being approximately 1·5 cm. (see fig. 2).

The object of using a square coil was to obtain, as far as possible, a closed magnetic circuit of the substances which were introduced, generally iron wire cores, as by this means calculation would be simplified.

With the assistance of Mr. Duddell, to whom the author is much indebted, a very sensitive measuring apparatus was arranged, with the permission of the late Prof. Ayrton, at the Central Technical College, for the measurement of this self-induction.

With this apparatus the value $L = 4{\cdot}1 \times 10^{-5}$ henrys was obtained correct to ± 1 per cent. for the single-layer coil. The resistance of this coil at 14° C. was 0·63 ohm. Another square coil was used to obtain lower frequencies; in this there were seven layers of wire on each side of the square, the whole containing 2670 turns of wire. The self-induction of this coil was also carefully measured with a secohmmeter, and found to be $5{\cdot}031 \pm 0{\cdot}012$ millihenrys. The resistance of the coil at 14·3° C. was 8·18 ohms. A third coil, used chiefly for preliminary experiments, consisted of a single bobbin of the same wire wound in seven layers; this contained 750 turns of wire, and had a self-induction of approximately 1 millihenry. Its self-induction was not measured by the secohmmeter, but was obtained by comparison with the square seven-layer coil by means of the air condenser. The results of these experiments are given later.

Measurement of the Plates.

5. In order to obtain accurate measurement of the spark photographs, a large measuring micrometer with a low-power microscope was used, with a cross wire in the eye-piece. In most cases it was found possible to obtain measurements of not very quickly damped sparks accurately to within 2 per cent., but with sparks whose period varied the accuracy was very much lower, as the black spots were often spread out and asymmetrical.

Theory of Experiments.

6. From the fundamental equations for the discharge of a condenser of C farads capacity through a coil of self-induction L henrys, and with a total resistance of R ohms in the circuit, the frequency of oscillation is given by

$$f = \frac{1}{2\pi}\sqrt{\left(\frac{1}{CL} - \frac{R^2}{4L^2}\right)}.$$

The current at any instant $= \dfrac{Q_0}{pLC} e^{-Rt/2L} \sin pt$ ampères,

where $\qquad p = 2\pi \times \text{frequency} \quad \text{and} \quad Q_0 = V_0 C,$

where V_0 is the P.D. on the spark gap just before discharge, measured in volts.

When the self-induction of the coil is variable, a graphical method of determining the frequency of oscillation has been used.*

Equation for the Induction in an Iron Core.

7. It will now be necessary to consider the case of a core of soft iron wires, which is magnetised by the rapidly alternating current flowing through the coil surrounding them. It may be assumed for simplicity that the cores of the square coil form a closed magnetic circuit.

In order to gain some idea of the way in which the magnetism dies away as it penetrates into the iron wire, the analysis for a single straight circular soft iron wire given by Sir J. J. Thomson† has been adopted. In a very fine wire, such as is used in the experiments under consideration, the cross magnetisation may be neglected.

The total flux (c) through the wire

$$= \left(\int_0^a \mathrm{A}\mathrm{J}_0(jnr)\, 2\pi r dr\right) e^{jpt}.$$

But $$\int r\mathrm{J}_0(jnr)\, dr = (jr/n)\, \mathrm{J}_0'(jnr),$$

from the known properties of Bessel functions.

Since $\mathrm{J}_0(0) = 0$, $$\mathrm{C} = \frac{2\pi ja}{n}\mathrm{J}_0'(jna)\,\mathrm{A}e^{jpt},$$

or, substituting for A, $$\mathrm{C} = \frac{2\pi\mu\mathrm{H}ja\mathrm{J}_0'(jna)}{n\mathrm{J}_0(jna)}e^{jpt}.$$

In calculating the value of C from this expression, the value $n^2 = 4\pi\mu jp/\sigma$ has been used, leakage being neglected.

Damping of Oscillations.

8. This is an important consideration, as the most marked effect produced by solid iron cores (or, in fact, solid cores of any metal) is the greatly increased damping of the oscillations; while even with fine iron wire cores the number of vibrations in many cases is reduced from 10 or 15 to 3 or 4.

According to the investigation given above the damping factor is $\mathrm{E}^{-\mathrm{R}t/2\mathrm{L}}$; and accordingly, as L increases, R remaining constant (the change caused by introducing the iron wire cores), R/2L is diminished, and hence the damping should be less rapid with the larger self-induction. It is clear, therefore, that

* 'Phil. Mag.,' January, 1903, p. 155.

† 'Recent Researches in Magnetism and Electricity,' p. 304.

the cause of the very rapid damping must be the absorption of energy by the cores introduced, either by hysteresis or by eddy currents, or both.

Using the same notation as above, in which the magnetic force is represented by the real part of H, the magnetic induction being assumed uniform along the axis of the wire, the rate of heat production per unit length of wire due to eddy currents is equal to the mean value of—

$$\tfrac{1}{2}a\left(\text{real part of } \frac{p}{n}\frac{J_0'(jna)}{J_0(jna)}\,\mu H e^{\iota pt}\right) H\cos pt,$$

where μ = magnetic permeability,

$p = 2\pi \times$ frequency,

σ = specific resistance of iron,

a = radius of iron wire.

When na is small the heat produced $= N/16\sigma\pi\mu^2p^2a^4H^2$* per unit length of core per second, N being the number of wires and H the maximum magnetising force.

The experiments of Sir J. J. Thomson (*loc. cit.*) appeared to show that the hysteresis of iron accounted for a considerable part of the absorption of energy.

In these experiments it will be shown that hysteresis loss is almost negligible as compared with eddy-current loss.

Results of Experiments.

Part I.

9. The first series of experiments† was made in order to find how nearly the frequency determined by experiment agreed with that calculated from the observed self-induction and capacities used in the tests.

The tests made with the air condenser may first be considered. The capacity of the air condenser was obtained both by calculation and by comparison with the standard ½-microfarad condenser. The capacity found in this way = 0·0102 microfarads. On account of the bending of the plates, it was found impossible to obtain a spark more than 0·6 mm. long, and some difficulty was found in photographing this, as well as in maintaining the discharge by the large Wimshurst machine.

A series of determinations was first made of the self-induction of the circuit apart from the coil. Using the small coil, the time for a complete

* 'Recent Researches in Electricity and Magnetism,' J. J. Thomson, p. 320.

† These results are not given at great length as the paper by Battelli and Magri ('Phil. Mag.,' June, 1903, p. 620) covers the subject quite fully.

oscillation of the circuit with the coil in position = T_c (see Table). The time for a complete oscillation without the coil = T_e.

	T_c (with coil).	T_e (without coil).	Ratio.
With Sets II–V of glass condenser	3·25	1·18	2·75
	3·25	1·16	2·80
Sets II–VIII of glass condenser	4·46	1·56	2·86

The mean value of T_c/T_e = 2·81.

Hence, calculating the self-induction of the circuit, $L_e = 0·6 \times 10^{-5}$ henry.

A typical result with the air condenser and large coil is given below:—

Self-induction = 5·03 millihenrys, which, with the self-induction of the circuit, gives a total self-induction = 5·036 millihenrys.

Capacity	0·0102 microfarad,
Theoretical time for a complete vibration......	$4·50 \times 10^{-5}$ sec.,
Length of half-oscillation on the plate	0·066 inch,
Time for 100 revolutions of the mirror.........	2·89 secs.,
Time for complete vibration	$4·45 \times 10^{-5}$ sec.

The agreement is within the limits of experimental error.

This measurement was repeated, in order to verify the result:—

Length of half-oscillation..................	0·0114 (mean of six readings),
Time for 100 revolutions of the mirror	1·68 secs.,
Time for complete vibration	$4·48 \times 10^{-5}$ sec.,

giving a still closer agreement.

An attempt was made to use the single-layer square coil, but it was not found possible to obtain a spark photograph which could be measured with any approach to accuracy. The results have not, therefore, been given.

10. A series of tests was made with the large glass condensers and the small coil, and the time of oscillation for each set of condensers carefully measured. These results are tabulated below:—

Number of sets of condensers.	K_r in microfarads.	$T \times 10^{-5}$.
I	0·137	1·58
I–II	0·279	2·28
I–III	0·415	2·76
I–IV	0·554	3·18
I–V	0·690	3·55
I–VI	0·82	3·84
I–VII	0·95	4·2
I–VIII..............	1·08	4·46
I–IX	1·22	4·68
I–X	1·35	5·06

In all these experiments the spark length was 2·5 mm. and the values of T are accurate to within 2 per cent.

11. In order to see whether the resistance of the circuit can have any effect on the frequency of the oscillations, the effective resistance (R_1) for the

wire has been calculated from the expressions originally given by Lord Rayleigh. For the highest frequencies used—

$$R_1 = 1{\cdot}18 \times (\text{resistance to steady current}).$$

Since $R = 0{\cdot}38$ ohm, $R_1 = 0{\cdot}45$ ohm.

For this frequency,

$$1/LC = 2{\cdot}6 \times 10^{11} \quad \text{and} \quad (R/2L)^2 = 0{\cdot}014 \times 10^{11}.$$

The effect of the resistance of the circuit in this case is therefore negligible.

For the lower frequencies, when using the single-layer square coil, the total resistance neglecting the spark may be taken $= 1$ ohm,

$$\frac{1}{LC} = \frac{10^{11}}{5{\cdot}7} \quad \text{and} \quad \left(\frac{R}{2L}\right)^2 = \frac{10^{11}}{670},$$

so that in this case also the correction is less than 1 per cent. When the coil is used with an iron core, the value of L is increased, and the correction will therefore be smaller still.

It will be shown later that when the maximum current during an oscillation of the spark falls to less than 200 ampères, the resistance of the spark increases to about 2 ohms, and may be expected to become larger still as the current through the spark diminishes still further. Under certain conditions, therefore, the spark resistance will have to be taken into account.

Part II.

12. The results of the experiments made to determine the effect of currents at high frequencies on iron may now be considered. With frequencies varying from 100,000 to 5000 per second, the effect of an iron or nickel wire core is to produce a spark discharge which has no constant frequency, but in which the period for a half-oscillation rapidly increases as the discharge becomes damped by energy absorption.* Having observed the effect, the explanation is obvious. It is clear that at these frequencies iron retains very much the same properties as it does under a steady magnetic field, *i.e.* the permeability of the iron increases as the flux density in the iron diminishes.

13. Experiments have been made with a variety of soft iron wire cores, and it will be convenient first to consider the effects produced with discharges from the set of ten large glass condensers through the single-layer coil, when the latter is arranged with an iron wire core.

* This phenomenon has now been observed by Battelli and Magri (*loc. cit.*).

The values of K_e in the above table have been used in the calculations, and the results are tabulated below.

t = time in seconds for 100 complete revolutions of mirror,

l_1 = length of quarter-oscillation from pilot spark at the beginning of the discharge to the first maximum current or blob on the plate,

l_2 = distance between first and second maxima,

l_3 = distance between second and third maxima,

l_4 = distance between third and fourth maxima, and so on.

The distances between the maximum values have been taken, as it was impossible to determine with any approach to accuracy the distance between successive minima.* To obtain the value of l_1', l_2', l_3', etc., which represent the lengths between successive zero values of current, the following method has been adopted. Taking first l_1 and l_2, (l_1+l_2) has been assumed to form the sum of three terms of an arithmetical progression, the first term of which is l_1, l_1' represents the sum of the first two terms.

The values of L_1, L_2, etc., are calculated from these figures.

The method of drawing the discharge curve already referred to,† when the B-H curve for the iron is known, has been applied in certain cases, and the result of one of these calculations is given in fig. 3.

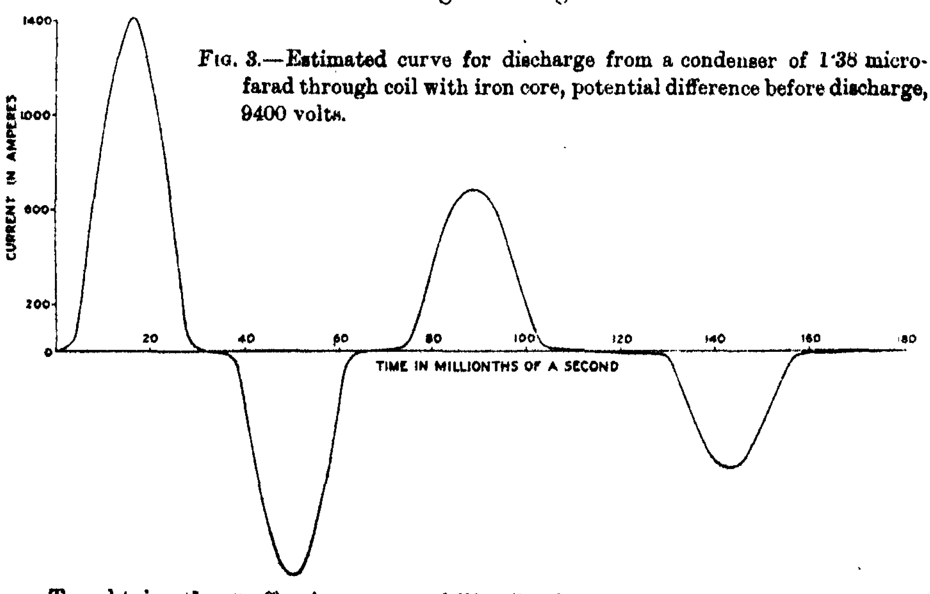


FIG. 3.—Estimated curve for discharge from a condenser of 1·38 microfarad through coil with iron core, potential difference before discharge, 9400 volts.

To obtain the "effective permeability" of the iron the lines of force may be assumed to be of uniform density; on the introduction of an iron

* The reason for this is clear from the curves drawn graphically in fig. 5.

† 'Phil. Mag.,' January, 1903, p. 155.

core a certain number of lines go through the iron. We may put, therefore, $L_0 = KA_0$, where A_0 is the area of one turn of the coil (calculated from the mean value of the self-induction) and K is a constant.

When a core is introduced $L = K[(A_0 - A_1) + \mu_e A_1]$, where A_1 is the area of the iron core, and μ_e is a quantity which may be designated the "effective" permeability.

Hence $$\mu_e = 1 + \frac{(L - L_0) A_0}{A_1 L_0}.$$

The quantity μ_e may be defined as the permeability of the iron which would give the same period of oscillation for the spark as is obtained experimentally, the "effective permeability" being constant and independent of the value of the magnetising force.

With the single-layer square coil $A_0 = 2{\cdot}29$ sq. cm.

			sq. cm.	
(1)	Area of section of the No. 28 S.W.G. iron wire core		$= 0{\cdot}64$.	$\frac{A_0}{A_1} = 3{\cdot}55$.
(2)	„ „ 18 „	„	$= 0{\cdot}70$.	$\frac{A_0}{A_1} = 3{\cdot}06$.
(3)	„ „ 24 „	„	$= 0{\cdot}61$.	$\frac{A_0}{A_1} = 3{\cdot}7$.
(4)	„ „ 28 „ nickel	„	$= 0{\cdot}58$.	$\frac{A_0}{A_1} = 3{\cdot}9$.

14. In the following table are shown the results obtained when the discharge from No. 1 set of the large condenser flows through the single-layer square coil into which a core [(1) above] made up of 550 No. 28 S.W.G. iron wires has been inserted, the spark gap is 2·5 mm., corresponding to a P.D. before discharge of 9400 volts.

Large condenser, No. I set.—$T_0 = 1{\cdot}58 \times 10^{-5}$ sec., $L_0 = 4{\cdot}1 \times 10^{-5}$,
$l = 0{\cdot}6 \times 10^{-5}$, volts $= 9400$, $t = 2{\cdot}26$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·03	0·068	$3{\cdot}6 \times 10^{-5}$	24·1	18·4
0·085	0·118	$6{\cdot}25 \times 10^{-5}$	73·0	60·0
0·17	(½)0·098	$10{\cdot}4 \times 10^{-5}$	195·0	164·0

15. In the first place, the value of the maximum current during the first half-oscillation was estimated, and was found to be 210 ampères.

The corresponding value of the magnetising force due to this current = 1000 C.G.S. units approximately.

The value of B corresponding to this, obtained from Ewing's results for Low Moor wrought iron $= 22 \times 10^3$, giving a value of $\mu = 22$ approximately, a result which is of the same order of magnitude as the effective permeability calculated above.

16. By the calculation made below, it will be seen that allowance for "skin" effect makes very little difference in the value of μ. Taking

$$\mu = 19, \qquad \sigma = 1{\cdot}2\times10^{5}, \qquad p = 1{\cdot}75\times10^{5},$$

from above, and making the necessary substitutions, the magnetic induction through a single wire

$$C = 0{\cdot}022\,H\cos pt-\phi, \quad \text{where} \quad \tan\phi = 0{\cdot}134,$$

giving an effective permeability which does not differ appreciably from 19.

This result shows, however, that there is a lag in the maximum induction through a wire, behind the magnetising force of about 9° on the assumption that the permeability of the iron is constant.

17. It will now be necessary to take into account the loss of energy during a half-oscillation of the spark.

The losses of energy may be classified under four heads :—

(1) Loss (of heat, light, and sound) in the spark itself.

(2) Loss of energy in the wires of the circuit due to the passage of the current (C^2R loss). (This is allowed for in the damping factor.)

(3) Loss of energy in the cores due to hysteresis of the iron.

(4) Loss of energy in the cores due to eddy currents.

The losses due to the spark, and to Joulian heat loss in the wires, occur in exactly the same way in discharges through coils having no cores (in which case there are usually 10 or more half-oscillations on the negative) as they do when iron cores are introduced, in which there are usually not more than two or three half-oscillations visible, with the smaller condensers. The main loss of energy for these discharges must therefore be sought in other directions. (With the discharges from the largest condenser a greater number of oscillations are visible with the iron cores in position, but for these discharges the ohmic loss is much more considerable.)

18. Considering first the losses due to hysteresis. The iron used for the core was very soft and well annealed, and, as a first approximation, a loss of 20,000 ergs per cubic centimetre for a complete cycle has been assumed, or 10,000 ergs for a half cycle. In making this assumption, the very high flux in the iron has to be taken into account, coupled with the statement of M. Klemencic* and others that the hysteresis loss is greater at high

* 'Wien. Akad. Sitzberg,' 1898, vol. 107, pp. 330–360. M. Klemencic seems to have determined the hysteresis loss by a determination of the decrement of current in a Leyden jar discharge. No allusion is made to corrections which have to be introduced for eddy current losses. See also Warburg and Hönig, 'Wied. Ann.,' vol. 20, p. 814; 'Phil. Mag.,' September, 1889; Battelli and Magri, 'Accad. Lincei Atti,' vol. 15, pp. 485–492; Corbino, 'Accad. Lincei Atti,' vol. 16, pp. 167–170; 'Atti dell' Assoc. Elett.,' vol. 7, p. 606; F. Piola, 'Elett. Romi,' vol. 5, pp. 4–6.

frequencies than low. Now, the total volume of the iron in the cores $= 62$ c.c. approx. Hence the total loss of energy due to hysteresis for the half-oscillation $= 0{\cdot}62 \times 10^6$ ergs. This loss is quite small as compared with the eddy-current losses.

The loss due to eddy currents during the first half-oscillation calculated from the formulæ given above $= 23{\cdot}8 \times 10^6$ ergs. Adding to this the hysteresis loss as calculated above, the total iron loss $= 2{\cdot}44 \times 10^7$ ergs. The ohmic loss due to the resistance of the coil is comparatively small. In this case, assuming the root mean square value of the current to be 0·707 of the maximum value, it amounts to $0{\cdot}4 \times 10^7$ ergs. for the first half-oscillation.

The total energy stored $= 5{\cdot}95 \times 10^7$ ergs.

The value given above shows that the eddy-current and hysteresis losses amount to more than one-third of the total energy of the discharge during the first half-oscillation, whereas the loss due to ohmic resistance is only 0·07 of the total energy.

The damping of the oscillations with iron cores might be expected to be much more rapid than when the cores are not present, and this is precisely what is observed. The total number of half-oscillations on the plate with the iron cores is three, whereas without them ten half-oscillations, and even more, have been photographed.

This result confirms the observation that the permeability of the iron is not very different at this frequency from that observed under similar conditions with a steady magnetising force, for, if the magnetic induction were very different from the value that has been assumed, the total calculated eddy-current loss would not have agreed so nearly with experiment.

19. The other results obtained with the set of large condensers may now be dealt with. These will correspond with lower frequencies than those considered in the preceding paragraphs. The results are tabulated according to the method described in § 13.

Large condensors, Nos. I–II.—$T_0 = 2{\cdot}28 \times 10^{-5}$, volts $= 9400$, $L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h.

l.	l'.	T.	$L \times 10^{-5}$.	μ_r.
0·029	0·067	$3{\cdot}9 \times 10^{-5}$	18·2	8·8
0·086	0·10	$5{\cdot}9 \times 10^{-5}$	31·0	24·5
0·1	0·167	$9{\cdot}7 \times 10^{-5}$	85·0	72·0
0·28	(¼)0·17	$20{\cdot}0 \times 10^{-5}$	362·0	310·0

Maximum current during first half-oscillation = 380 ampères.
Maximum magnetising force ,, ,, = 1880 C.G.S. units.

Large condensers, Nos. I–III.—Capacity = 0·385 mf., $T = 2·76 \times 10^{-5}$, volts = 9400, $L_0 = 4·1 \times 10^{-5}$ h., $l = 0·6 \times 10^{-5}$ h., $t = 2·4$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·041	0·092	$5·2 \times 10^{-5}$	16·0	11·3
0·112	0·125	$7·0 \times 10^{-5}$	30·1	23·0
0·13	0·164	$9·2 \times 10^{-5}$	52·0	42·0
0·22	(½)0·125	$14·0 \times 10^{-5}$	120·0	100·0

Maximum current during first half-oscillation = 480 ampères.
Maximum magnetising force „ „ = 2070 C.G.S. units.

Large condenser, Nos. I–IV.—$T_0 = 3·18 \times 10^{-5}$, volts = 9400, $L_0 = 4·1 \times 10^{-5}$ h., $l = 0·6 \times 10^{-5}$ h., $t = 3·17$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·081	0·075	$5·5 \times 10^{-5}$	13·5	9·5
0·101	0·114	$8·4 \times 10^{-5}$	32·0	25·0
0·114	0·131	$9·7 \times 10^{-5}$	43·0	35·0
0·164	(½)0·091	$13·4 \times 10^{-5}$	83·0	68·0

Maximum current during first half-oscillation = 530 ampères.
Maximum magnetising force „ „ = 2550 C.G.S. units.

Large condenser, Nos. I–VI.—$T_0 = 3·84 \times 10^{-5}$, volts = 9400, $L_0 = 4·1 \times 10^{-5}$ h., $l = 0·6 \times 10^{-5}$ h., $t = 3·13$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·084	0·076	$5·6 \times 10^{-5}$	9·4	5·6
0·09	0·099	$7·2 \times 10^{-5}$	16·0	11·3
0·105	0·114	$8·3 \times 10^{-5}$	21·5	16·0
0·126	0·148	$10·8 \times 10^{-5}$	36·5	29·0
0·18	(½)0·098	$14·3 \times 10^{-5}$	64·0	54·0

Maximum current during first half-oscillation = 770 ampères.
Maximum magnetising force „ „ = 3700 C.G.S. units.

Large condenser, Nos. I–X.—$T_0 = 5·06 \times 10^{-5}$, volts = 9400, $L_0 = 4·1 \times 10^{-5}$ h., $l = 0·6 \times 10^{-5}$ h., $t = 3·1$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.	Maximum magnetising force.	T for complete oscillation, estimated from curve in fig. 6.
0·04	0·089	$6·45 \times 10^{-5}$	7·0	3·5	5250 gauss	$6·4 \times 10^{-5}$
0·107	0·116	$7·7 \times 10^{-5}$	10·1	6·3	3100 „	$7·2 \times 10^{-5}$
0·115	0·131	$9·5 \times 10^{-5}$	16·0	11·3	1900 „	$8·4 \times 10^{-5}$
0·16	0·194	$14·0 \times 10^{-5}$	25·4	19·4	950 „	$13·4 \times 10^{-5}$
0·23	0·272	$19·7 \times 10^{-5}$	70·0	58·0	(?) 420 „	
0·33	(½)0·17	$24·6 \times 10^{-5}$	110	93		

Estimated maximum magnetising force first half-oscillation = 5250 C.G.S. units.

Considering, in the first instance, the first half-oscillation of the spark after the discharge begins, it will be noticed that when iron cores are introduced the change in frequency produced by using different capacities is comparatively slight, varying from 28,800 ∼ per second with 0·137 microfarad to 18,800 ∼ per second with 1·35 microfarad. It will also be noticed that the decrease of effective permeability with increase of capacity is not quite uniform, but this is amply accounted for by possible errors in observation.

A curve has been plotted between the values of the effective permeability and maximum magnetising force, and is shown in fig. 4.

20. Considering next the half-oscillations of the spark other than the first

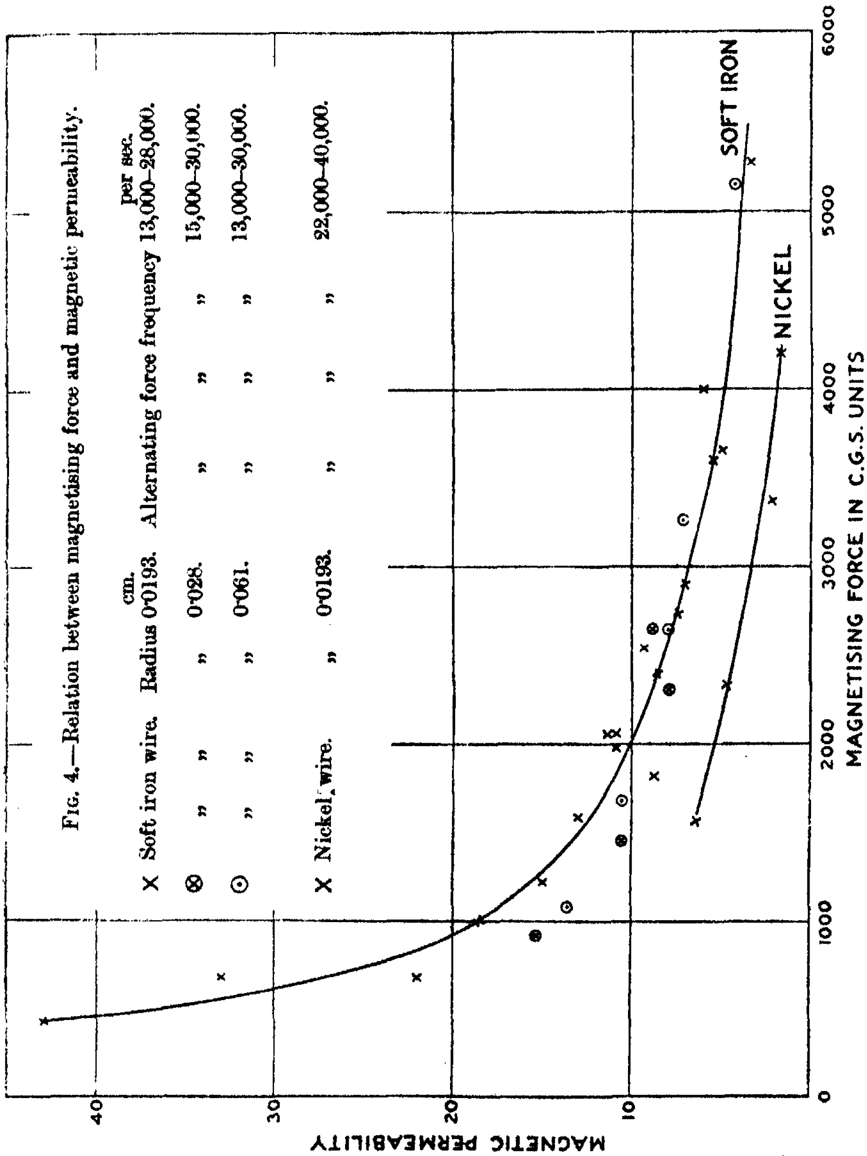


FIG. 4.—Relation between magnetising force and magnetic permeability.

it will be seen that the same law holds. Increase in capacity diminishes the apparent effective permeability. Thus the second half-oscillations with 0·137 microfarad corresponds with a greater value of the effective permeability.

It is noticeable from these figures that the damping of the discharge is

much less rapid with the larger capacities, the number of oscillations visible with the larger condenser being nearly as great with as without iron cores in the coil. This is due to the great increase in the relative importance of the ohmic losses with the larger condenser. Taking, for example, the discharge from the condenser with a capacity of 1·35 microfarads, the ohmic loss during the first half-oscillation is approximately 16×10^7 ergs, whereas the eddy-current loss in the core is less than that calculated in § 18, and is approximately 2×10^7 ergs.

The resistance loss in the circuit is therefore the predominant factor in determining the decrement of the spark, and it is only at the end of the spark that eddy-current loss becomes important. The great ohmic loss was also noticeable from the fact that after two or three discharges with the large condenser the coil became perceptibly warm. The discharge curve for this condenser has been drawn by the method already mentioned (see fig. 3),* the eddy-current loss being taken into account by suitably reducing the voltage at the beginning of each half-oscillation when drawing the curve. The times for a complete oscillation have been determined from the curve, and are tabulated with the results found experimentally. These figures agree within limits of experimental error with the spark photographs, and confirm the fact that the permeability of the iron at these frequencies is not very different from that under steady conditions. It will be noticed that the maximum current calculated on the assumption that sine waves are being dealt with is over 25 per cent. less than that estimated by the graphical analysis.

The figures calculated from the formula for the maximum magnetising current have been used in drawing the curves in fig. 3, and these are the values given in the tables. The root mean square or virtual current estimated from the graphical curves differs in most cases by not more than 6 per cent. from that obtained by assuming the "calculated" current to be of sine wave shape.

From the results obtained with the largest condenser an attempt has been made to determine the magnitude of the resistance of the spark itself.

From the values calculated from the "effective" permeability the corresponding value of "H" for each half-oscillation of the spark can be found, and hence the maximum value of the current, assuming a sine wave shape for the curve as a first approximation. From this value for the current, the maximum voltage at the condenser at the beginning of each half-oscillation has been determined, and hence the loss of energy during each half-oscillation

* The values of spark resistance referred to later have been taken account of in drawing this curve.

has been estimated. These results are tabulated below. The loss in energy during each half-oscillation has been assumed to be due to (1) ohmic resistance, (2) eddy current in the core, (3) hysteresis in the core. Dielectric hysteresis in the glass has not been taken into account. The total for these losses is also shown in the table below. If a spark resistance of 0·5 ohm is assumed, the losses are increased to the values shown in the last column, which agree quite closely with those calculated from the loss in voltage by the condenser. Although too much value should not be attached to the actual figure assumed for the resistance of the spark, it shows that with currents of this magnitude, the resistance is not large enough to cause any perceptible difference in the frequency of the oscillation.*

Large condenser, I–X.—Capacity 1·38 microfarad.

	Estimated value of H.	Estimated voltage at beginning of oscillation.	Loss in energy during half-oscillation.	Estimated total loss neglecting spark resistance.	Estimated total loss assuming spark resistance = 0·5 ohm.
1st half-oscillation	5250	9400	$33 \cdot 5 \times 10^7$ ergs.	$19 \cdot 3 \times 10^7$ ergs.	$33 \cdot 0 \times 10^7$ ergs.
2nd " "	3100	6300	$12 \cdot 4 \times 10^7$ "	$10 \cdot 2 \times 10^7$ "	$13 \cdot 6 \times 10^7$ "
3rd " "	1900	4680	$6 \cdot 9 \times 10^7$ "	$5 \cdot 26 \times 10^7$ "	$6 \cdot 9 \times 10^7$ "
4th " "	950	3400	$4 \cdot 9 \times 10^7$ "	$2 \cdot 50 \times 10^7$ "	$3 \cdot 0 \times 10^7$ "
5th " "	420 q.p.	2100			

N.B.—If the value of the spark resistance for the 4th half-oscillation be assumed equal to 2 ohms, the total energy loss during the 4th half-oscillation becomes $4 \cdot 9 \times 10^7$ ergs.

Similar calculations have been made on other typical discharges, in particular, with the discharge of a condenser of 1 microfarad at an initial potential difference of 7800 volts; the average resistance for the spark which it is necessary to assume to bring the energy losses into agreement is 0·48 ohm at 770 ampères, 0·76 ohm at 440 ampères, and 1·2 ohms at 230 ampères. The accuracy of these figures is not great, and they are of value as showing the order of magnitude of the quantity involved, and in this respect they confirm the results which have been given above.

21. Experiments were made in order to determine how the spark length, and, consequently, the potential difference at the spark gap just before the discharges, affected the observed effect. It is clear that a shorter spark will give a smaller maximum current during the first half-oscillation, and hence, according to the above results, the apparent self-induction of the coil should be increased. Below are given the results obtained with spark gaps 2 mm. and 1·5 mm. in length.

* This result is in accordance with that obtained by Battelli and Magri, 'Phil. Mag.,' June, 1903, vol. 5, pp. 620–643.

Using the notation of § 13—

Large condenser, No. I.—$T_0 = 1{\cdot}58 \times 10^{-5}$ sec., $L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 1{\cdot}64$ sec., volts before discharge = 7800.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·05	0·101	$3{\cdot}9 \times 10^{-5}$	28	22·4
0·104	(½)0·004 (?)	$4{\cdot}1 \times 10^{-5}$	31	25·5

Maximum current during first half-oscillation = 140 ampères.
Maximum magnetising force „ „ = 670 C.G.S. units.

Large condensers, Nos. I–II.—$T = 2{\cdot}28 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4{\cdot}1 \times 10^{-5}$, $l = 0{\cdot}6 \times 10^{-5}$, $t = 2{\cdot}26$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·04	0·09	$4{\cdot}8 \times 10^{-5}$	20·2 henry	15
0·12	0·15	$8{\cdot}0 \times 10^{-5}$	57·0 „	47
0·18	(½)0·103	$10{\cdot}9 \times 10^{-5}$	117·0 „	99

Maximum current during first half-oscillation = 255 ampères.
Maximum magnetising force „ „ = 1220 C.G.S. units.

Large condensers, Nos. I–IV.—$T_0 = 3{\cdot}18 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 1{\cdot}92$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·062	0·131	$5{\cdot}9 \times 10^{-5}$	15·6	11
0·152	0·18	$8{\cdot}1 \times 10^{-5}$	30·0	23
0·22	(½)0·12	$10{\cdot}8 \times 10^{-5}$	54·0	44

Maximum current during first half-oscillation = 430 ampères.
Maximum magnetising force „ „ = 2070 C.G.S. units.

Large condensers, Nos. I–VI.—$T_0 = 3{\cdot}84 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}10$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·062	0·124	$6{\cdot}1 \times 10^{-5}$	11·2	7·0
0·126	0·141	$6{\cdot}9 \times 10^{-5}$	14·6	10·2
0·168	0·191	$9{\cdot}4 \times 10^{-5}$	28·0	21·0
0·264	(½)0·15	$14{\cdot}6 \times 10^{-5}$	67·0	56·0

Maximum current during first half-oscillation = 600 ampères.
Maximum magnetising force „ „ = 2890 C.G.S. units.

Large condensers, Nos. I–VIII.—$T_0 = 4{\cdot}46 \times 10^{-5}$ sec., volts = 7800, $L = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}06$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.	H.
0·06	0·129	$6{\cdot}2 \times 10^{-5}$	8·5	4·9	3700
0·146	0·163	$7{\cdot}9 \times 10^{-5}$	14·0	9·5	2180
0·178	0·204	$9{\cdot}8 \times 10^{-5}$	22·0	17·0	1100
0·24	0·319	$15{\cdot}3 \times 10^{-5}$	54·0	48·0	450
0·44	(½)0·251	$24{\cdot}2 \times 10^{-5}$	137·0	120·0	—

Maximum current during first half-oscillation = 775 ampères.
Maximum magnetising force „ „ = 3700 C.G.S. units.

A similar series of results was obtained with a 1·5 mm. spark gap.

Large condenser, No. I.—$T_0 = 1{\cdot}58 \times 10^{-5}$ sec., volts = 6150,
$L = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}36$.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·048	0·097	$5{\cdot}36 \times 10^{-5}$	53	43
0·098	(½)0·049	$5{\cdot}4 \times 10^{-5}$	54	44

Maximum current during first half-oscillation = 92 ampères.
Maximum magnetising force „ „ = 440 C.G.S. units.

Large condenser, Nos. I–II.—$T_0 = 2{\cdot}28 \times 10^{-5}$ sec., volts = 6150,
$L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}38$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·06	0·122	$6{\cdot}8 \times 10^{-5}$	54·1	33
0·126	(½)0·064	$7{\cdot}1 \times 10^{-5}$	45·0	36

Maximum current during first half-oscillation = 140 ampères.
Maximum magnetising force „ „ = 670 C.G.S. units.

Large condensers, Nos. I–IV.—$T_0 = 3{\cdot}18 \times 10^{-5}$ sec., volts = 6150,
$L = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}31$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·048	0·117	$6{\cdot}3 \times 10^{-5}$	18	13
0·158	0·19	$10{\cdot}3 \times 10^{-5}$	49	40
0·21	(½)0·11	$11{\cdot}9 \times 10^{-5}$	65	54

Maximum current during first half-oscillation = 330 ampères.
Maximum magnetising force „ „ = 1580 C.G.S. units.

Large condenser, Nos. I–VI.—$T_0 = 3{\cdot}84 \times 10^{-5}$ sec., volts = 6150,
$L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}52$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·06	0·12	$7{\cdot}1 \times 10^{-5}$	15·4	10·8
0·12	0·139	$8{\cdot}2 \times 10^{-5}$	21·0	15·6
0·176	0·207	$12{\cdot}2 \times 10^{-5}$	47·0	38·0
0·228	(½)0·12			

Maximum current during first half-oscillation = 410 ampères.
Maximum magnetising force „ „ = 1980 C.G.S. units.

Large condenser, Nos. I–VIII.—$T_0 = 4{\cdot}46 \times 10^{-5}$ sec., volts = 6150,
$L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}48$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·06	0·13	$7{\cdot}5 \times 10^{-5}$	12·6	8·5
0·150	0·17	$9{\cdot}8 \times 10^{-5}$	22·0	16·0
0·20	0·24	$14{\cdot}8 \times 10^{-5}$	51·0	41·0
0·29	0·36	$20{\cdot}8 \times 10^{-5}$	101·0	86·0
0·48	(½)0·27 ?	$31{\cdot}0 \times 10^{-5}$	225·0	193·0

Maximum current during first half-oscillation = 500 ampères.
Maximum magnetising force „ „ = 2400 C.G.S. units.

Large condenser, Nos. I–X.—$T_0 = 5{\cdot}06 \times 10^{-5}$ sec., volts = 6150,
$L_0 = 4{\cdot}1 \times 10^{-5}$ h., $l = 0{\cdot}6 \times 10^{-5}$ h., $t = 2{\cdot}5$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·06	0·14	$8{\cdot}2 \times 10^{-5}$	11·7	7·5
0·18	0·19	$11{\cdot}1 \times 10^{-5}$	22·0	16·6
0·19	0·21	$12{\cdot}3 \times 10^{-5}$	27·0	21·0
0·23	0·26	$15{\cdot}2 \times 10^{-5}$	42·0	34·0
0·30	(½)0·16	$18{\cdot}7 \times 10^{-5}$	63·0	52·0

Maximum current during first half-oscillation = 570 ampères.
Maximum magnetising force „ „ = 2750 C.G.S. units.

22. It is obvious from the above results that the important factor to be taken into consideration is the maximum current during the first half-oscillation; the points on the curve in fig. 4 plotted from these results agreeing fairly closely with those obtained from the first series of experiments. The variation in the depth to which the magnetism penetrates is relatively unimportant. It is to be noticed, however, that the amount of penetration depends on the permeability, and also on the frequency. Hence the magnetisation will penetrate into the iron and give a more nearly uniform distribution of magnetisation with the larger condenser.

23. The effect of using different diameters of wire for the cores may now be considered.

Below are given some of the results of a series of experiments made with a soft iron core consisting of 60 No. 18 wires. Area of iron $= A_1 = 0.70$ sq. cm. The same notation is adopted as in § 13.

Large condenser, No. I.—$T_0 = 1.58 \times 10^{-5}$ sec., volts $= 9400$, $L_0 = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.81$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·04	0·08	3.4×10^{-5}	21	13·6
0·08	(½)0·04	3.4×10^{-5}	21	13·6

Maximum current during first half-oscillation = 225 ampères.
Maximum magnetising force " " = 1080 C.G.S. units.

Large condenser, Nos. I–II.—$T_0 = 2.28 \times 10^{-5}$ sec., volts $= 9400$, $L_0 = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.81$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·05	0·013	4.35×10^{-5}	16·6	10·5
0·011	(½)0·057	4.8×10^{-5}	20·2	13·0

Maximum current during first half-oscillation = 245 ampères.
Maximum magnetising force " " = 1660 C.G.S. units.

Large condenser, Nos. I–X.—$T_0 = 4.68 \times 10^{-5}$ sec., volts $= 9400$, $L = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.92$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_e.
0·064	0·145	6.5×10^{-5}	8·5	4·4
0·178	0·209	9.4×10^{-5}	18·2	11·4
0·24	(½)0·127	11.4×10^{-5}	26·0	17·2

Maximum current during first half-oscillation = 1070 ampères.
Maximum magnetising force " " = 5150 C.G.S. units.

24. These results appear, at first sight, somewhat remarkable, as it will be seen, on comparing them with the results obtained with a core composed of much finer wire, No. 28 S.W.G., that there is very little difference in the value of μ_e in the tables. On comparing the areas of the surface of the wires per centimetre length of the core, it is seen that, whereas for the No. 28 core the surface is 64·8 sq. cm., the surface for the No. 18 core is only 22·6 sq. cm.;

and since it is the surface of iron in the core which would appear to be most important, it might be expected that the change in frequency produced by the core would be much less noticeable.

The explanation, however, is obvious. With the larger diameter wire core the loss due to eddy currents is greatly increased. According to the approximate formula given above (§ 8) it depends on the fourth power of the diameter,* and hence the loss of energy during the first half-oscillation would be more than ten times as great for a core having the same amount of iron in it, and made of the No. 18 wire, as it would be for one of No. 28 S.W.G. wire. The actual magnetising current rapidly falls off, therefore, on account of this loss in energy.

There is another effect tending to diminish the magnetising force inside the iron, what is called the self-demagnetising force due to the magnetisation on the surface of the wire, at the place where the magnetic lines leak. This self-demagnetising force is increased with increase in diameter of the wire.

The diminution in the magnetising force owing to these causes will correspond with a greater permeability in the iron, which (although the increase in permeability of the iron diminishes the depth to which the magnetisation penetrates) is sufficient to counterbalance the much greater surface of iron exposed, with the finer core. As in this case the permeability must clearly be higher than in the previous cases, we may assume (taking into account the ratio of the surfaces), as a first approximation, $\mu = 30$.

[As the results obtained with the large condenser, No. I, seem to be in very fair accordance with those given for the other sparks, the result for the first half-oscillation has been used as a basis of calculation.]

Proceeding exactly as in § 16,

$$\mu = 30, \qquad p = 1{\cdot}84 \times 10^5, \qquad \sigma = 1{\cdot}2 \times 10^4.$$

Hence
$$n^2 = 5800j, \qquad a = 0{\cdot}061 \text{ cm.}$$

The total induction through the core

$$= 8{\cdot}46\,\mathrm{H}\cos(pt-\phi), \qquad \tan\phi = 0{\cdot}85,$$

since the area of the iron $= 0{\cdot}70$ sq. cm. This gives a value for the effective permeability $\mu_e = 12{\cdot}1$, instead of $\mu_e = 13{\cdot}6$ as found by experiment.

It is of interest to observe the comparatively great lag in the maximum magnetic induction behind the maximum magnetising force. With these

* The radius of the finer wire No. 28 is 0·0193 cm., and of the No. 18 wire is 0·061 cm. The energy loss for the same mass of iron will be proportional to the squares of the diameters of the wires.

cores this lag is just over 40°. It should be remembered, however, in connection with this calculation that the permeability has been assumed constant, a condition very different from that which actually exists.

The actual loss of energy calculated from the approximate expressions given above gives a loss greater than the total energy stored in the condenser, which confirms the experimental observation that damping with these cores must be extremely rapid.

25. A third series of determinations has been made using cores made up of 250 No. 24 S.W.G. soft iron wires, in which it might be expected that the effects observed would be intermediate between those found with cores of larger and smaller diameter. The results have been arranged below in the same way as the previous ones.

The notation of § 13 has been adopted.

Large condenser, No. I.—$T_0 = 1.58 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.29$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_c.
0·050	0·11	3.3×10^{-5}	20	15·4
0·12	(½) (0·06)	3.6×10^{-5}	24	19·0

Maximum current during first half-oscillation = 190 ampères.
Maximum magnetising force „ „ = 910 C.G.S. units.

Large condenser, Nos. I–II.—$T_0 = 2.28 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4.1 \times 10^{-5}$, $l = 0.6 \times 10^{-5}$ h., $t = 1.6$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_c.
0·052	0·110	4.1×10^{-5}	14·6	10·6
0·132	0·064	4.8×10^{-5}	20·0	15·4

Maximum current during first half-oscillation = 305 ampères.
Maximum magnetising force „ „ = 1460 C.G.S. units.

Large condenser, Nos. I–IV.—$T_0 = 3.18 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.56$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_c.
0·061	0·143	5.2×10^{-5}	12·0	8·0
0·184	0·19	6.9×10^{-5}	21·5	16·4
0·19	(½)0·20	7.3×10^{-5}	24·1	19·0

Maximum current during first half-oscillation = 480 ampères.
Maximum magnetising force „ „ = 2300 C.G.S. units.

Large condenser, Nos. I–VI.—$T_0 = 3.84 \times 10^{-5}$ sec., volts = 7800, $L_0 = 4.1 \times 10^{-5}$ h., $l = 0.6 \times 10^{-5}$ h., $t = 1.60$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_c.
0·08	0·173	6.5×10^{-5}	12·8	8·8
0·20	0·216	8.1×10^{-5}	20·0	15·4
0·22	0·238	8.5×10^{-5}	22·4	18·0
0·34	(½)0·123	9.2×10^{-5}	26·0	21·0

Maximum current during first half-oscillation = 550 ampères.
Maximum magnetising force „ „ = 2650 C.G.S. units.

The value of A_1, the area of iron in this core, is equal to 0·61 sq. cm.

26. It will be seen that the values of the effective permeabilities hardly differ from those given in previous paragraphs for cores composed of finer and thicker wires; the permeability is slightly less than with the fine wire cores, and greater than with the thicker wire cores. It is obvious also that the absorption of energy due to eddy-current losses is intermediate between that observed with the thicker and thinner wires.

Taking $\mu = 25$, $a = 0{\cdot}028$ cm., and $H = 910$ C.G.S. units, the loss of energy during the first half-oscillation is $7{\cdot}5 \times 10^7$ ergs.

The total energy of the discharge in this case, however, is reduced to $3{\cdot}9 \times 10^7$, since the potential difference between the coatings of the condenser was only 7800 volts, and as in the case of the No. 18 core, the calculated eddy-current loss is too large, because allowance is not made for the penetration of the flux to the centre of the wire, and for the rapid dying away of the current.

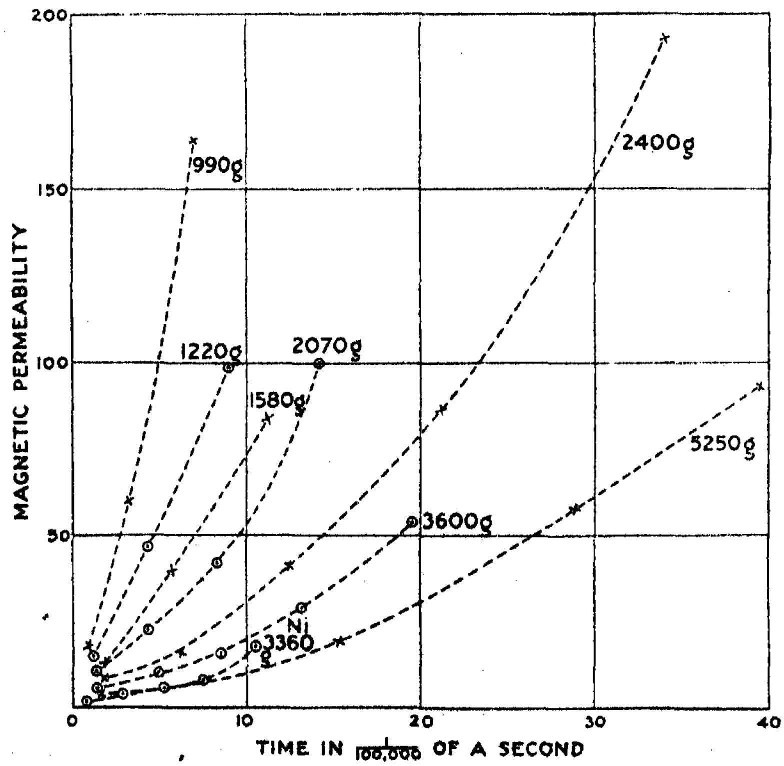


FIG. 5.—Curves showing increase in permeability during successive oscillations of discharge (from condenser) of iron wire (No. 28 B.W.G.) core placed in coil through which discharge passes.

Numbers opposite curves are maximum magnetising forces during first half-oscillation.

27. The results obtained for the three different sets of iron cores have all been plotted on the same sheet (fig. 4). The curves in fig. 5 have been drawn to show the way in which the effective permeability increases from the beginning of the discharge in one or two typical cases, the abscissæ representing time, and the ordinates "effective permeability." The maximum values are shown plotted against the time from the beginning of the discharge corresponding to the given maximum.

Effect of Size of Core.

28. An investigation was also made to determine, if possible, the depth to which the magnetisation penetrated into the core, *i.e.* to find out if the inner wires were screened by the outer layers; to this end, a series of cores were made up, consisting of wooden centres, round which were placed layers of iron wire.

With No. 28 wire, one set of cores was made up with a single layer placed round the inner core of mahogany, 85 wires being used.

A second set was made up of three layers of wires placed round a central wooden core, 220 wires being used.

A third core was made up of 24 No. 18 wires placed round a central core of wood.

It will be obvious that with a smaller volume of iron in the cores the accuracy of the calculation of the "effective permeability" of the iron will be very much reduced. For instance, the ratio of iron to air in the core with the 85 No. 28 wires is as 1 : 23 only, so that, in order to calculate the effective permeability of the core, the alteration in the self-induction of the coil must be determined with far greater accuracy than in the case in which the ratio of the iron to air is 1 : 3·5, as with the original cores.

With the No. 28 wire cores the general tendency of the results is to show that the induction through the outer layers is greater than through the central cores, with the No. 18 wires the effect was somewhat more marked, but the possible accuracy is so low that the numerical results are of little value.

Part III.—*Nickel Wire Cores.*

29. Besides the experiments made on iron as described in Part II, a series of discharges through coils having cores of nickel wire was photographed, the results from which are tabulated below. It will be seen that the phenomena are similar to those obtained with iron cores, though the effects are less marked with the nickel wires. The core consisted of 500 No. 28 wires, $A = 0·58$ sq. cm.

Using the notation of (§ 13)—

Large condenser, No. I.—$T_0 = 1 \cdot 58 \times 10^{-5}$ sec., volts $= 9400$, $L_0 = 4 \cdot 1 \times 10^{-5}$ h. $l = 0 \cdot 6 \times 10^{-5}$ h., $t = 1 \cdot 31$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_r.
0·036	0·077	$2 \cdot 35 \times 10^{-5}$	9·8	6·5
0·086	0·093	$2 \cdot 85 \times 10^{-5}$	14·7	11·1
0·096	0·097	$3 \cdot 0 \times 10^{-5}$	16·6	13·1
0·100	(?)0·05			

Maximum current during first half-oscillation = 825 ampères.
Maximum magnetising force „ „ = 1560 C.G.S. units.

Large condenser, Nos. I–II.—$T_0 = 2 \cdot 28 \times 10^{-5}$ sec., volts $= 9400$, $L_0 = 4 \cdot 1 \times 10^{-5}$ h., $l = 0 \cdot 6 \times 10^{-5}$ h., $t = 1 \cdot 65$ sec.

l.	T.	$L \times 10^{-5}$.	μ_r.
0·08	$3 \cdot 1 \times 10^{-5}$	8·1	4·9
0·084	$3 \cdot 2 \times 10^{-5}$	8·7	5·3
0·088	$3 \cdot 4 \times 10^{-5}$	10·0	6·7
0·108	$4 \cdot 2 \times 10^{-5}$	15·4	12·0
0·14	$5 \cdot 4 \times 10^{-5}$	26·0	21·0

Maximum current during first half-oscillation = 485 ampères.
Maximum magnetising force „ „ = 2330 C.G.S. units.

Large condenser, Nos. I–VI.—$T_0 = 3 \cdot 84 \times 10^{-5}$, volts $= 7800$, $L_0 = 4 \cdot 1 \times 10^{-5}$ h., $l = 0 \cdot 6 \times 10^{-5}$ h., $t = 1 \cdot 60$ sec.

l.	l'.	T.	$L \times 10^{-5}$.	μ_r.
0·044	0·110	$4 \cdot 1 \times 10^{-5}$	4·7	1·7
0·124	0·128	$4 \cdot 8 \times 10^{-5}$	6·7	3·3
0·128	0·14	$5 \cdot 2 \times 10^{-5}$	8·0	4·9
0·14	0·14	$5 \cdot 2 \times 10^{-5}$	8·0	4·9
0·14	0·15	$5 \cdot 6 \times 10^{-5}$	9·4	6·1
0·18	0·24	$9 \cdot 0 \times 10^{-5}$	25·0	21·0
0·28	0·15	$11 \cdot 2 \times 10^{-5}$	39·0	34·0

Maximum current during first half-oscillation = 880 ampères.
Maximum magnetising force „ „ = 4200 C.G.S. units.

30. We may proceed in exactly the same way as in the case of the No. 28 iron wire cores to determine more exactly the actual permeability necessary to produce the observed results, making allowances for the "skin effect."

First, calculating the value of n,

μ may be assumed $= 7$ as a first approximation,

$$p = 2 \cdot 67 \times 10^5,$$

$$\sigma = 1 \times 10^4 \text{ C.G.S. units},$$

whence $n^2 = 2350j, \qquad a = 0 \cdot 0193$ cm.

Hence the magnetic induction through a single wire $= 0 \cdot 0082 \cos(pt - \phi)$, where $\tan\phi = 0 \cdot 112$, giving an effective permeability which does not differ appreciably from 7. The lag in maximum magnetic induction behind maximum magnetising force is $6\frac{1}{2}^\circ$ neglecting hysteresis.

Calculating next the eddy-current losses, we may again take the approximate expression given above.

The energy lost during the first half-oscillation

$$= 1{\cdot}29 \times 10^7 \text{ ergs},$$

the total energy of the discharge being $5{\cdot}93 \times 10^7$ ergs as before.

The loss of energy is about half that with iron wires of the same diameter, and the damping of the oscillations would therefore be expected to be much less rapid than with an iron wire core, and this result is shown experimentally by the spark photographs, the number of oscillations visible on the plate being approximately twice as large as with iron wire cores.

The results for nickel, therefore, may be said to have the same general characteristics as those obtained with iron, though the effects produced both on the frequency and the damping of the oscillations is less marked.

Cores of Other Materials.

31. Some of the early experiments made to verify the first observation of the variable frequency spark may now be considered.*

An experiment was made using a battery of 14 Leyden jars and a six-layer coil having a self-induction of rather less than 1 millihenry, in order to make certain that the effects observed with the iron cores were entirely due to the iron, and not to any other cause. For this purpose a core was made of insulated copper wire (No. 28 S.W.G.) and coated with shellac exactly as was done with the iron wire cores; this was inserted in the coil described above, but not the slightest change in frequency could be observed, and the number of oscillations visible on the plate was not greatly reduced.

Time for a complete oscillation without cores	$4{\cdot}01 \times 10^{-5}$ sec.
„ „ „ with copper wire cores...	$3{\cdot}96 \times 10^{-5}$ „

The agreement between these results is clearly within limits of experimental error.

When a similar core of iron wires was inserted, all the characteristic effects both of change of frequency and of damping were observed.

When a core of solid brass was introduced, the time for a complete oscillation $= 3{\cdot}54 \times 10^{-5}$ seconds, thus showing an increase in frequency as found by Hemsalech.†

With a solid soft iron core the number of half-oscillations visible on the plate is reduced to two, thus showing the very great eddy-current loss; while

* Results published by Hemsalech confirm some of these observations. 'Journ. d. Phys.,' 1908, pp. 76–90; 'Comptes Rendus,' vol. 140, pp. 1322–1325.

† 'Comptes Rendus,' vol. 140, pp. 1322–1325.

the time for a complete oscillation $= 4{\cdot}4 \times 10^{-5}$ seconds. This appears to indicate a slight decrease in frequency, due to the permeability of the iron.

With the solid iron core, the permeability, therefore, is sufficiently great to overcome the effect of eddy currents, and tends to increase the self-induction, and to produce a slight decrease in the frequency.

32. It may be of interest here to notice some experiments in which a coil similar to the above was wound on a brass tube, about 1/32 inch thick. In this case the brass seemed to screen off the action of the iron entirely, and no difference whatever could be observed when the iron cores were introduced, either in damping or in change of frequency, this result is also in agreement with that obtained by Hemsalech using a tube of zinc (*loc. cit.*).

Conclusions.

General.

1. With an air condenser, the capacity of which was measured ballistically, and an air-core self-induction coil of known value, the frequency of the oscillations of the condenser discharge agrees (within limits of experimental error) with the values calculated by Kelvin's formula.

2. The resistance of a spark between spheres of 1 inch diameter, 2·5 mm. apart, has been estimated; the resistance of such a spark when the maximum current is greater than 200 ampères does not exceed 2 ohms. If the maximum current through the spark is greater than 500 ampères, the resistance does not exceed 0·75 ohm.

Effects Produced by an Iron Wire Core in the Self-induction.

3. When an iron wire is inserted in the self-induction coil, the time for each consecutive half-oscillation increases with the duration of the discharge.

4. With a series of discharges from a given condenser in which the maximum value of the magnetising current varies, the time for the first half-oscillation *decreases* with *increase* in the strength of the current.

5. The increase in the time of a half-oscillation with the duration of the discharge is due to the increase in the permeability of the iron, as the current, and consequently the magnetising force, dies away.

6. The permeability of the iron wires calculated from the observed increase in the self-induction of the coil, decreases with increase of the magnetising force. The curve connecting μ the "effective" permeability, with H, the magnetising force, agrees, within limits of experimental error, with that obtained on the assumption that the permeability of the iron is the same as it is under a steady magnetising force.

7. When an iron wire core is inserted into the self-induction coil the discharge is more quickly damped than with no core. This is due to eddy-current and hysteresis losses, the former being the more potent.

Effect of Variation of the Diameter of the Wire of the Core.

8. The "effective" permeability of thick wires, 0·12 cm. in diameter, is nearly equal to that of thin wires subjected to the same magnetising force (*i.e.* between the limits of 500–5000 gauss).

This is due to a balancing of the three effects stated below :—

(1) The increase in the "skin" effect with thick wire diminishes the apparent permeability.

(2) The maximum value of the magnetising force is reduced, in consequence of the increased dissipation of energy with thick wires, thus increasing the apparent permeability.

(3) The self-demagnetising force due to leakage from the surface of the wire decreases the actual magnetising force acting on the iron, thus increasing the permeability of the iron.

9. With cores of solid iron inserted into the self-induction coil the duration of the discharge is less than with any other cores ; the self-induction of the coil with solid iron cores is generally slightly (about 15 per cent.) greater than with air cores.

Effects Produced by Cores of other Materials.

10. Nickel wire cores produce similar effects to those observed with iron, but of diminished intensity, the permeability of the nickel wire with rapidly oscillating magnetic force being similar to that found with steady magnetising forces.

11. With cores made up of insulated copper wires, no changes, either in damping or self-induction, are apparent.

In conclusion, the author's best thanks are due to the late Lord Blythswood for the loan of the apparatus described above, and to the late Lord Kelvin for the kind encouragement given by him during the early stages of the research, to Mr. Duddell for the measurements of the self-induction of the various coils used, and for his criticisms, and to Dr. Silvanus Thompson for his criticisms and suggestions.

Load-Extension Diagrams taken with the Optical Load-Extension Indicator.

By W. E. Dalby, City and Guilds Engineering College.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received January 24,—Read February 13, 1913.)

[Plates 2 and 3.]

This paper may be regarded as a continuation of that communicated in January, 1912,* wherein I described a new optical apparatus by means of which it is possible to obtain load-extension diagrams free from the inertia effects of the parts of the testing machine in which the materials are strained and broken.

The apparatus is automatic in its action and gives a true record of the physical properties of the materials. The curve corresponding to the straining and breaking of a specimen is drawn by means of a spot of light moving over a photographic plate placed in the camera which forms part of the instrument. There is no practical limit to the speed at which a diagram can be taken other than that imposed by the "rapidity" of the plate.

When fracture of a specimen takes place, the spot moves across the plate so rapidly that no impression is made, and hence the actual load carried by the specimen at the instant of fracture is determined without ambiguity, because the spot of light ceases to record at the instant of fracture. Even if a plate were used so rapid that the quick movement of the spot across the plate after fracture of the specimen were brought out, the discontinuity in the curve and the difference in intensity would fix the point accurately.

This property of the instrument, namely, its power of recording the true load-extension curve at any speed of loading, opens up a new field of research in the subject of the strength of materials, as is indicated below by the results obtained by the almost instantaneous straining of a piece of mild steel beyond its elastic limit.

The diagrams given in my previous paper related to mild steel, iron, and copper. The present paper relates to the physical properties of gun-metal, brass, and phosphor-bronze, as disclosed by their respective load-extension diagrams and the corresponding micro-photographs of their molecular structure; to further experiments on mild steel, with the instrument arranged somewhat differently in order to magnify the extension so much that the photographic record exhibits the elastic part of the diagram; and

* 'Roy. Soc. Proc.,' A, vol. 86, p. 414.

also to diagrams obtained by the application of load so quickly that the straining of the material up to the elastic limit may almost be regarded as done by an impulsive load.

Group 1.—Copper-Tin and Copper-Zinc Alloys.

A piece of *phosphor-bronze* which was turned to a diameter of 0·54 inch was broken in the testing machine by a load applied so that the rate of straining was approximately constant. The composition of the specimen was:—Copper, 89·7 per cent.; tin, 8·85 per cent.; lead, 1·21 per cent.; phosphorus, a trace.

The load-extension diagram is shown in fig. 1, together with the microphotograph showing the structure of the material. The magnification is 1500 diameters. (See Plate 2.)

The form of this diagram is in marked contrast to the form obtained from mild steel. There is no period of molecular instability between the breaking-down point and the plastic yielding, as in the case of mild steel. The curve is smooth and continuous from the commencement of the loading to the point of fracture. There is a quasi-elastic stretching of the material up to a load of about 7 tons, followed by a plastic yielding with a continually falling load.

Reckoned on the original area of the bar, the load at fracture corresponds to a stress of 22·9 tons per square inch. The reduction of area at the point of fracture was, however, 69 per cent. of the original area of the bar, so that the actual load carried by the bar at the instant of fracture was 74 tons per square inch. The extension of the bar measured on a gauge length of 5 inches was 9·4 per cent.

The peculiar scythe-shaped diagram of this material is different in almost every respect from the characteristic diagrams obtained from iron and steel.

Gun-Metal.—A load-extension diagram from a specimen of gun-metal is shown in fig. 3 and the corresponding microphotograph in fig. 4; magnification, 750 diameters; diameter of specimen, 0·6 inch; distance between the gauge points, 5 inches. The composition of the metal was:—Copper, 85·4 per cent.; tin, 12·4 per cent.; lead, 2·41 per cent.

There is a general resemblance in form between the curves in figs. 3 and 1, but the gun-metal has a considerably increased plastic limb. The quasi-elastic line in each diagram is very much the same in character, but the difference between the maximum load and the breaking load is not so great in the gun-metal as in the phosphor-bronze specimen.

The stress on the gun-metal specimen at the instant of fracture, reckoned on the original area of the bar, was 21·2 tons per square inch, but reckoned

on the actual area corresponding to a reduction of area of 55 per cent., it was 45·8 tons per square inch, considerably lower than in the case of phosphor-bronze. On the other hand the extension on 5 inches was 14 per cent., considerably greater than in the extension of phosphor-bronze. It is noteworthy that a not very great difference in chemical composition of the two materials results in a considerable difference in the physical properties.

Brass.—The load-extension diagram of a piece of brass rod is shown in fig. 5, and the corresponding microphotograph in fig. 6. Fig. 7 shows the load-extension diagram of a second specimen cut from the same brass rod, and fig. 8 shows the corresponding microphotograph. The magnification in both figs. 6 and 8 is the same, namely, 190 diameters. The first specimen (fig. 5) was tested just as it was cut from the rod. The second specimen (fig. 7) was annealed in a muffle furnace before testing. The specimen was heated to a dull red, and then allowed to cool in the furnace, the cooling lasting about four hours. (See Plate 3.)

Comparing the two load-extension diagrams together and also the two corresponding microphotographs together, it will be seen that the process of annealing has exerted a marked influence on the physical properties and on the molecular structure of the material. In fact, the annealing process has destroyed entirely the quasi-elastic part of the load-extension diagram. Whereas the unannealed bar carried a load of nearly 7 tons before passing into the plastic state, the annealed bar begins to approach that state before a load of 2 tons is reached. Further, if the diagram for the annealed bar is compared with the load-extension curve of the copper bar given in my previous paper it will be seen that there is a striking resemblance in form. The resemblance is so close that at a first glance the load-extension diagram of the annealed brass bar would be mistaken for a diagram from a copper bar. The composition of the bar is as follows:—Copper, 58·6 per cent.; zinc, 40·8 per cent.; lead, 0·6 per cent.

There is a marked contrast also in the crystalline structure. In the unannealed state (fig. 6) the metal appears to be constructed of two kinds of material, roughly equal in size and uniformly distributed; the lighter areas represent one kind of crystal, and the darker areas another kind. After annealing (fig. 8), it will be observed, the dark areas have grown and the lighter areas have almost disappeared. The magnification is the same in each figure, hence it is clear that the substance represented by the darker area has grown into aggregates of relatively large size. These large aggregates seem to indicate that the long period of annealing has probably resulted in the formation of a true eutectic alloy.

Another peculiar characteristic of brass will be seen on the diagrams for both the annealed and the unannealed specimen, namely, the peculiar discontinuities in the curve as the specimen draws out. These discontinuities appear earlier on the diagram of the unannealed specimen than on that of the annealed specimen. The bar itself gives evidence that the internal stress has been somewhat differently distributed than in the case of the other metals tested, because after it has been drawn out to a length approaching the breaking-point the bar is no longer round but veined. To the hand it feels as though the original smooth, circular, and apparently homogeneous bar has been drawn out into a bundle of thick strings.

The effect of annealing is also shown by comparing the ultimate stress and elongation of the specimens, though the annealed specimen extended so much that the end of the curve did not appear on the plate; consequently the actual load at fracture could not be measured.

	Unannealed.	Annealed.
Percentage elongation on 5 inches	20·0	42·4
Percentage reduction of area	18·8	46·0
Maximum load per square inch carried by the bar, reckoned on the original area	29·2	25·7 tons.
Load per square inch carried by the bar, reckoned on the actual area at fracture	42·8	

A common characteristic of all the alloys tested was the absence of a true elastic modulus. The load line begins to bend away very soon after extension begins.

Mild Steel Specimen Broken with Suddenly Applied Load.

One of the most interesting diagrams I have ever taken with the apparatus is that shown in fig. 9. A mild steel specimen was put with the apparatus into the shackles of a 30-ton testing machine. The straining cylinder of the machine was connected directly to the hydraulic main of the works. The accumulators were pumped to the top of their strokes, and the pumps were then stopped. The regulating valve on the testing machine admitting water to the straining cylinder was then opened wide, as quickly as it was possible to turn it, with the result that the whole break occupied only 10 seconds. Notwithstanding this extremely rapid break, the whole of the load-extension diagram was obtained with the apparatus, with the exception of just the end, which came off the plate. Everything worked perfectly, and after the fracture the spot of light came back to its initial position.

Although the whole period of the break was small, namely 10 seconds,

the time occupied by the purely elastic extension was a very small fraction of the whole time. This is indicated by the relative intensity of the line in the elastic and in the plastic part of the diagram in the actual photograph. The time occupied by the elastic extension was certainly less than 1/10 second.

Fig. 10 is placed beside fig. 9 for the purpose of comparison. The curve is the load-extension diagram of a second specimen cut from the same bar as that from which the specimen broken in 10 seconds was cut, the load-extension diagram of which is shown in fig. 9. The time occupied in breaking this second bar was $2\frac{1}{2}$ minutes. The effect of the rapidity of the straining on the apparent properties of the material can be estimated by a comparison of the two figures.

Each bar was 0·55 inch diameter, and in each case the gauge points were 5 inches apart. The scale of extension is practically the same in each case, namely, $3\frac{3}{4}$ to 1, whilst the load scale is just the same, and is practically 1 ton = 9 mm. on the original diagrams.

The following results are found by measurement from the diagrams and the bars.

	10-second break (fig. 9).	150-second break (fig. 10).
Original diameter	0·55 in.	0·55 in.
Original area	0·238 sq. in.	0·238 sq. in.
Fractured area	0·071 „	0·084 „
Reduction of area	70 per cent.	65 per cent.
Gauge length	5 in.	5 in.
Extension	1·45 in.	1·22 in.
Elongation	29 per cent.	24·4 per cent.
Maximum load reckoned on the original area of the bar	26·5 tons per sq. in.	25·2 tons per sq. in.
Load at yield point	25·2 „ „	24·0 „ „

Comparing these results, it will be seen that the rapidity of breaking has little effect on either the yield-point or the maximum loads, but has a more marked effect on the plastic properties of the material. With quick loading the extension of the material on 5 inches increases from 24 to 29 per cent., and the reduction of area is increased from 65 to 70 per cent.

A third specimen cut from the same bar was broken in 9 seconds, and the curve obtained was essentially the same as that shown in fig. 9.

Load-Extension Diagrams of the Elastic Part of the Curve.

A specially designed extensometer and a modified arrangement of the instrument were used to obtain a diagram of just the elastic part of the

curve. Fig. 11 shows a diagram taken from a piece of mild steel in which the extension is so magnified by the instrument that only 0·01 inch extension appears on the diagram. The scale of extension is such that 2·1 inches on the diagram represents an actual extension of 0·01 inch of the specimen. By measurement of this diagram it was found that the bar extended 0·0804 inch on 5 inches for a change of load of 6 tons, the area of the bar being 0·282 square inch. From these data E = 13,240.

A similar diagram is shown in fig. 12 for a piece of electrolytic copper. From this it appears that copper has no true modulus of elasticity, since it begins to curve away directly the load is applied. It would almost appear that for materials of this kind another definition of the modulus of elasticity should be used, if the term is used at all. For example, it might be defined as the ratio between unit stress and unit strain measured from a tangent at the origin of the diagram.

The difficulty of taking diagrams with this great magnification of the extension is chiefly that, with the ordinary testing appliances, it is difficult to get a true axial pull on the specimen. For this kind of work it is necessary to use the device of crossed knife-edges instead of the ordinary spherical joints usually found in testing machines.

The diagrams shown in this and the preceding paper sufficiently illustrate the use of the apparatus as an instrument of research in determining the strength of materials, and indicate that many lines of investigation may be followed in connection with the determination of the physical properties of materials.

Summarising the points of advance made:—

(1) The diagrams are obtained free from inertia of the heavy mass of the beam of the testing machine and the jockey weight usually used as part of an autographic recording apparatus.

(2) Pencil friction is entirely eliminated, since the diagram is obtained by the movement of a spot of light over a photograph plate, the movement of the spot being determined by small angular displacements of small light mirrors.

(3) The load on the specimen is measured by a weigh-bar placed in series with it. A variation of 1 ton on the specimen causes an elongation of about 0·001 inch on the weigh-bar. This movement is multiplied by the mirror and beam of light to a movement of about 1 cm. on the photographic plate.

(4) An extensometer is placed on the bar to measure its extension, and up to the elastic limit the specimen extends a distance of the order 0·01 inch on a 5-inch length. This movement is multiplied by a mirror and beam of light to about 4 cm. on the photographic plate.

(5) The accuracy of the multiplication and the sensitiveness of the mirror

gear and extensometer are shown by the results obtained in fig. 11. Fig. 11 may be regarded as a refined test of the instrument, since the slightest deviation from true proportionality in the multiplying mechanism of the instrument would be apparent on the elastic curve of a piece of mild steel. As shown on the diagram, the line is straight and has a slope which gives an elastic modulus known to be correct from independent measurements.

The accuracy of the instrument being established by this test, the accuracy of the curve in fig. 12 for copper, which was obtained by the instrument, is also established.

(6) The accuracy with which the instrument will follow the quick variations of stress in the specimen, that is to say, the freedom of the apparatus from lag due to inertia of the parts, is indicated by the diagram fig. 9, which shows how every detail of the variation of load and corresponding extension is brought out, even when the loading is so rapid that it is almost impulsive. The elastic part of the curve in this figure was described in certainly less than 0·1 second. From other evidence I know that the instrument will follow quicker variations than this, the first limit to the speed being the speed of the plate.

(7) The elastic line is drawn by the instrument continuously without a stop. An elastic line plotted from observations in the usual way is drawn through points which correspond to periods of dead loading. The loading is, in fact, intermittent, a stop being necessary at each load added to measure with an extensometer the elongation produced by the load.

(8) In the diagrams of the whole curve up to the break, as in fig. 10, the load on the bar at the instant of fracture is recorded.

Comparison of the Physical Characteristics of the Materials Tested.

When compared together the diagrams of gun-metal, brass, phosphor-bronze, copper, steel, and iron show two distinct parts: the elastic or quasi-elastic part, and the plastic part. There is, however, a sharp distinction between the alloys of copper, tin, and zinc and irons and steels. The distinction lies in the manner in which the material passes from the elastic into the plastic state. In the case of pure copper and its alloys, it is impossible to say where the elastic state ends and the plastic state begins. The elastic diagrams of the alloys of copper, tin, and zinc all show a quasi-elastic line (a line which in fact may almost be mistaken for an elastic line in those diagrams which show the whole of the break) with a perfectly smooth join on to the plastic part.

With the iron and steels, the elastic part of the diagram ends not quite suddenly but with a quick change into a curve where there appears to be

some struggle going on in the bar between the broken crystals, a struggle which apparently is settled, after an extension of about 0·1 inch, in favour of a predominating plastic partner. The curves obtained from annealed and unannealed brass rod, when considered with the micro-photographs and the curve from pure copper, show that the plastic properties of the materials are profoundly modified by the size of the aggregates from which the material is built up. And if steel is assumed to be an alloy of iron constructed of iron aggregates of large size through which is distributed a network of crystalline structure, the peculiar characteristic diagram which is always obtained from steel may be explained on the assumption that it is the resultant load-extension diagram of two separate materials, the one material being present as a hard crystalline structure, the other being the iron with which it is associated. The material breaks down in the elastic sense when this crystalline network gives way, but it continues yielding in the plastic sense and even carries a greater load than was carried at the time the network failed before local yielding begins. The giving way of the crystalline network is probably only a slip of the crystals, because, as is well known, annealing in boiling water appears to restore the elastic properties of the bar, though this boiling does not cause the bar to return to its original length, it merely permits the reconstitution of the network into a resisting system in the new relative position of the crystals produced by the first slip. It would be interesting to obtain the diagram of a piece of chemically pure iron. The load-extension diagram would probably be the same in character as that of pure copper.

I should like finally to express my thanks to Mr. W. H. Merrett, of the Royal School of Mines, for making the micro-photographs which are used to illustrate the paper.

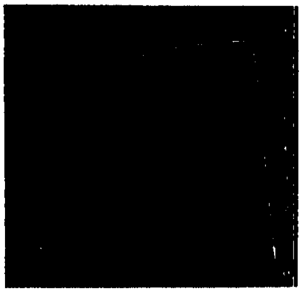


Fig. 1.

Fig. 2.

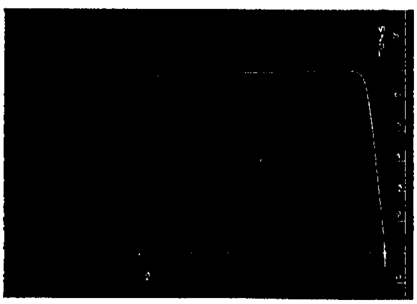


Fig. 3.

Fig. 4.

Fig. 9.

Fig. 10.

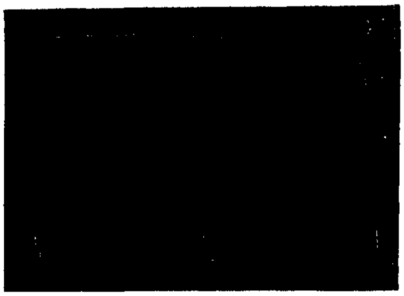


Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

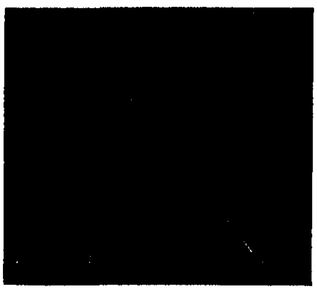


Fig. 11.

Fig. 12.

On a Fluorescence Spectrum of Iodine Vapour.

By Prof. J. C. McLennan.

(Communicated by Sir J. Larmor, F.R.S. Received March 11,—Read April 17, 1913.)

(Plate 4.)

In a number of most interesting papers Prof. R. W. Wood* has shown that it is possible to obtain from iodine vapour at ordinary room temperatures, under the stimulation of light from the mercury arc, a fluorescence spectrum, consisting of a number of lines ranging from $\lambda = 7005{\cdot}5$ Å.U. to $\lambda = 5337{\cdot}63$ Å.U. Further, he has shown that these lines can be divided into three series, one of which is stimulated by the light from the green line $\lambda = 5460{\cdot}74$ Å.U., another by the light from the yellow line $\lambda = 5769{\cdot}60$ Å.U., and a third by the light from the yellow line $\lambda = 5790{\cdot}66$ Å.U.

Up to the present, he has identified in his photographs some 23 members in the series stimulated by the mercury green line, 10 members in that excited by the yellow line of shorter wave-length, and 13 members in the series arising from the excitation of the yellow line of greater wave-length. Moreover, by using apparatus of high resolving power, he has recently been able to show that in nearly every case the members of the green line series are complex and are in reality close doublets accompanied by a number of fainter companions.

The members of the series due to the yellow line $\lambda = 5769{\cdot}60$ Å.U. are also complex, he finds, but they appeared as doublets when a Cooper Hewitt arc was used as the source of the stimulating light, and as triplets when the light from a quartz-mercury arc lamp was used as the source of excitation. The series of lines stimulated by the line $\lambda = 5790{\cdot}66$ Å.U. he also finds to be complex, but the constitution of the members of this series is not uniform, some of them being single lines, others doublets, and one even a triplet.

The three lines $\lambda = 5460{\cdot}74$ Å.U., $\lambda = 5769{\cdot}60$ Å.U., and $\lambda = 5790{\cdot}66$ Å.U., which Prof. Wood used in his investigation, as is well known, are among the strongest in the mercury arc spectrum, and the absence of any resonance lines of wave-lengths shorter than $\lambda = 5337{\cdot}63$ Å.U. suggests that, possibly, had a more intense source been used, or a modification in the method of illumination been adopted, some evidence might have been obtained of the excitation of additional series of resonance or fluorescence lines by the light

* R. W. Wood, 'Phil. Mag.,' Oct., 1911, p. 469, and Oct., 1912, p. 673.

from other lines in the mercury arc spectrum, and especially by that from the stronger lines in the ultra-violet region. In view of the possible existence of such an excitation, it seemed to the writer worth while to see if any indication of such resonance or fluorescence spectra could be obtained, and the following paper gives a short account of some experiments arranged with that end in view.

First of all, however, it seemed advisable to repeat Prof. Wood's experiments, and efforts were directed to see if any improvement could be made in the method of illumination used by him, so as to reduce, if possible, the time of exposure to obtain good photographs. After trying a number of arrangements, it was found that very satisfactory results could be obtained by illuminating the iodine vapour by the light from a number of Cooper Hewitt mercury arc lamps, placed parallel to each other and as close together as possible. Each of these lamps, it is known, furnishes a luminous discharge from 50 to 60 cm. in length, and when from four to six of them are used one can very conveniently obtain an exceedingly powerful illumination, as well as one of considerable extent.

With this arrangement it was found that very good results could be obtained with about two hours' exposure, and fig. 1, Plate 4, is an example of a photograph obtained with this arrangement in that time. The iodine vapour was contained in a highly exhausted glass tube, about 70 cm. long and 3 cm. in diameter, which was illuminated by the light from four Cooper Hewitt lamps, placed parallel to it and as close to it as they could be set up. The photograph was taken with a Hilger constant deviation spectroscope, with the collimator directed towards the rounded end of the iodine tube. The figure shows quite clearly the resonance lines stimulated by the green line, and a number of the members of the two series due to the two yellow lines.

Several plates were taken similar to this one with two-hour exposures, and they all showed quite clearly 20 out of the 23 members cited by Prof. Wood as belonging to the green-line series. On most of them, however, it was possible to make out only seven members of each of the series stimulated by light from the two yellow lines. This was owing in part to their relative faintness, and in part, at least in the case of several members of the series, to their close proximity to the relatively much stronger lines stimulated by the light from the green line. No doubt, with the use of screens to cut out this latter series, and with exposure of longer duration than two hours, the yellow line series could have been brought out with much more distinctness; but, in view of a point of special interest cropping up in another direction in the course of the work, the investigation of this matter was deferred for a time.

The point referred to came out while using a tube for illuminating

purposes, whose form is shown in fig. 2. It consisted of an outer part AHC made of glass of the ordinary Cooper Hewitt design, and a second part DB made of clear fused quartz which was sealed into the former by wax joints

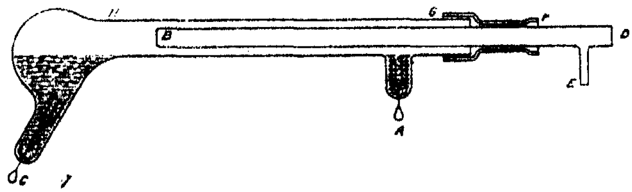


FIG. 2.

at G and F. The glass tube was furnished with mercury terminals at A and C, and carried the mercury arc. Iodine in crystals was inserted in the tube BD, which was then highly exhausted and afterwards sealed off at E.

With this apparatus it was possible to subject the iodine vapour in the inner tube to intense illumination by light whose wave-lengths extended beyond $\lambda = 7000$ Å.U. and down to approximately $\lambda = 1850$ Å.U.

On examining the light emitted by the tube containing the iodine vapour by means of a quartz spectrograph directed at the exposed end D, it was found that in addition to the ordinary mercury lines coming from the arc in the outer tube the spectrum contained a number of narrow bands extending from about 4600 Å.U. down to about 2100 Å.U. With exposures of two or three minutes these bands could be readily seen on the photographs, but exposures of 15 minutes brought them out more clearly. With an hour's exposure they were brought out still more distinctly, but on increasing this to two hours it was found that the density of the bands was not greatly enhanced.

A photograph of the spectrum illustrating the distribution of these bands is shown in Plate 4, fig. 3, A. This shows a set of seven well marked bands between $\lambda = 3341{\cdot}7$ Å.U. and $\lambda = 3131{\cdot}7$ Å.U., and also sets approximately equally spaced on either side of the line $\lambda = 4358{\cdot}3$ Å.U. A limited series of bands in pairs is distinguishable between $\lambda = 3131{\cdot}7$ Å.U. and $\lambda = 2893{\cdot}7$ Å.U., and a number of single bands can be seen between $\lambda = 2893{\cdot}7$ Å.U. and $\lambda = 2536{\cdot}7$ Å.U. Below $\lambda = 2536{\cdot}7$ Å.U. the bands are spaced at intervals of approximately 20 Å.U., and can be seen extending down to the limit of the photograph. The bands vary somewhat in width, but a majority of them have a width of approximately 10 Å.U.

A close examination was made of a number of photographs, and it was found possible to pick out over 80 bands in this new spectrum. The positions of these were determined as closely as possible by comparison with

the more prominent of the mercury lines and their approximate mean wave-lengths are given in Table I.

Table I.

Approximate mean wave-lengths of bands in Ångström units.	Remarks.	Approximate mean wave-lengths of bands in Ångström units.	Remarks.
4608	From λ = 4608 Å.U. to λ = 3365 Å.U. the bands are faint in places and the grouping is somewhat irregular.	2900	In the region from λ = 2900 Å.U. to λ = 2545 Å.U. the bands are quite distinct, but their spacing is irregular.
4550		2883	
4505		2853	
4452		2825	
		2799	
4290		2774	
4250		2760	
4210		2737	
4170		2727	
4130		2715	
		2697	
4015		2685	
3925		2667	
3870		2638	
3800		2628	
3725		2622	
3625		2617	
3585		2612	
3555		2594	
3520		2590	
3475		2580	
3445		2560	
3420		2545	
3395			
3365		2515	The bands below λ = 2515 Å.U. are spaced at intervals of about 20 Å.U., and each band is about 10 Å.U. in width.
		2495	
3315	The group of seven bands between λ = 3315 Å.U. and λ = 3175 Å.U. are particularly well marked and appear to be equally spaced at intervals of about 24 Å.U.	2476	
3290			
3268		2450	
3245		2426	
3220		2408	
3195		2382	
3175		2360	
		2340	
3107		2320	
3090		2300	
		2277	
3065	There are four well-marked pairs of bands in the region between λ = 3065 Å.U. and λ = 2915 Å.U.	2254	
3047		2237	
3009		2218	
2993		2195	
2960		2179	
2946		2162	
2930		2148	
2915		2129	

After obtaining the new band spectrum in the manner described, the tube BD was opened and air admitted. The iodine was then all dissolved with methyl alcohol and thoroughly washed out of the tube. The latter was then carefully freed of all moisture by forcing through it a current of dry air. Finally, it was exhausted once more and sealed up again. The mercury arc

was re-established in the outer tube, and photographs taken with the spectrograph again directed at the end of the tube D. One of these is shown in Plate 4, fig. 3, B. The bands, it will be seen, are entirely absent, and the only lines which are in evidence are those of the ordinary well-known mercury arc spectrum.

The disappearance of the band spectrum with the removal of the iodine vapour made it clear that the spectrum had its origin in this vapour. It did away, moreover, with the possibility of ascribing the spectrum to any fluorescence of the quartz tube under a stimulation by the ultra-violet light of the arc, or to a fluorescence of any mercury vapour which might have found its way in minute proportions into the iodine tube during the process of its evacuation by the mercury pump.

After having ascertained in the manner just described that the iodine vapour was the origin of the band spectrum, an experiment was made to see if the spectrum could still be obtained if the tube BD were provided with a window of crystalline quartz attached with sealing-wax or mastic at D. This was done to make certain that the mastic or wax of the joint did not give off any gas even in small quantities which might act upon the iodine vapour and so lessen its power to emit the band spectrum. When the end of the tube was cut off at D and the crystalline quartz window attached in its place, it was found, on repeating the experiment, that the bands, and, in fact, the mercury lines, too, came out with even greater clearness than when the end of the tube was made of fused quartz.

In the next experiment the tube was modified by making the portion BD of ordinary combustion glass tubing and providing it with a window of crystalline quartz, sealed on at D in the manner just described. After inserting the iodine crystals in the tube and exhausting it and sealing it off at D, the arc was struck in the outer tube and an exposure made with the quartz spectroscope, as before. In these experiments, although they were made repeatedly, no trace was obtained at all of the band spectrum. This will be seen from Plate 4, fig. 3, C, which is taken from one of the photographs obtained with this glass modification of the original tube.

The mercury lines come out quite distinctly down to $\lambda = 2893 \cdot 7$ Å.U., it will be seen, but there is not the slightest indication of any bands in the region immediately to the right or to the left of the line $\lambda = 4358 \cdot 3$ Å.U., or in the region between $\lambda = 3341 \cdot 7$ Å.U. and $\lambda = 3131 \cdot 7$ Å.U., while in both of these regions in fig. 3, A, the bands stand out most distinctly. Moreover, in none of the plates was there any indication of bands in that part of the spectrum lying below $\lambda = 2893 \cdot 7$ Å.U.

This interesting result shows, in the first place, that the emission of the

band spectrum by the iodine vapour could not have been due to an elevation of the temperature of the vapour by the heat from the arc, for the experimental conditions for obtaining a temperature spectrum were precisely the same with the combustion glass tube closed by a quartz window as with the fused quartz tube closed by the same window.

It is known from the experiments of Könen,* Friedrichs,† Puccianti,‡ Evans,§ and others that iodine vapour, when heated in an exhausted tube, emits a band spectrum at temperatures ranging about the same as the temperature of the iodine vapour in the tubes used in this investigation, but this temperature spectrum appears to be entirely confined to the region above that of the spectrum obtained in the present experiments, and so does not appear to have any direct relation to it.

It seems, therefore, that one must conclude that the emission of this new band spectrum by the iodine vapour is a true resonance or fluorescence effect stimulated by the light from one or more lines in the mercury arc spectrum (doubtless in the ultra-violet region) to which the combustion glass tubing is not transparent.

Up to the present, it has not been possible to pick out, with any certainty, the lines in the ultra-violet spectrum of the mercury arc which emit the light which gives rise to this new resonance or fluorescence spectrum from the iodine vapour. Owing to its strong intensity, however, the line $\lambda = 2536{\cdot}7$ Å.U. seems to be a likely one. The experiments of Hughes‖ indicate that a line or lines of comparatively strong intensity exist in the spectrum of mercury near the region $\lambda = 1850$ Å.U., and as quartz is still transparent to light of this wave-length, it is possible that the light from such line or lines may contribute, in part at least, to the effect.

It is known that mercury vapour absorbs the light of wave-length $\lambda = 2536{\cdot}7$ Å.U., and it should not be difficult to use this fact to see if the new resonance bands are excited by the light from this line or by the light from the lines close to it. By a modification of the tube shown in fig. 2 it should be quite easy to insert a third exhausted tube of fused quartz containing a little mercury between the quartz tube BD and the glass one AHC. With the arc established in AHC this intermediate tube would be heated, the mercury in it would become vaporised, and so as a vapour act as a screen to cut off the light emitted by the lines at and in the neighbourhood

* Könen, 'Wied. Ann.,' 1898, vol. 65, p. 297.

† Friedrichs, 'Zeit. für Wissen. Photographie,' 1905, vol. 3, p. 154.

‡ Puccianti, 'Atti della Reale Accademia dei Lincei,' 1905, vol. 14, 1st semestre, p. 84.

§ Evans, 'Ast. Phys. Journ.,' July, 1910, p. 1.

‖ Hughes, 'Camb. Phil. Soc. Proc.,' 1912, vol. 16, p. 428.

of $\lambda = 2536 \cdot 7$ Å.U. from the iodine vapour. By the use of this third tube, therefore, with mercury vapour or other absorbing medium in it, there should be no great difficulty in locating, with considerable definiteness, the region or regions in the spectrum of the mercury arc from which the light comes which stimulates the iodine vapour to the emission of this somewhat extensive band spectrum. Experiments with this end in view are now being carried out, and it is expected that information will soon be obtained which may throw some light upon this point.

A matter of interest in connection with these experiments is the complete absence from the plates, obtained with the new type of tube, of any indication of the lines belonging to the resonance or fluorescence spectrum from iodine vapour which has been so fully investigated by Prof. Wood. The explanation of this absence, however, seems evident. The tube BD, as is shown in fig. 2, projected for some distance beyond the end of the tube AHC. In consequence of this there would be a temperature gradient in the iodine vapour contained in it, the hottest portion being at the end B and the coldest at the other end. If the light from the mercury green and yellow lines stimulated the iodine vapour, or any part of it, at the heated end to the emission of the spectrum studied by Prof. Wood, the light which constitutes this spectrum would have to pass through a considerable column of comparatively cool iodine vapour before it fell upon the slit of the spectroscope. These are just the conditions under which one should expect to obtain an absorption of the resonance or fluorescence lines, and consequently their absence from the plates should not cause any surprise.

This explanation gains support, too, from the fact that there was considerable absorption by the iodine vapour of light corresponding to the green and the yellow lines of the mercury arc, for these appeared by visual observation very much sharper and narrower when viewed through the spectroscope with the iodine vapour in the tube BD than they did when this vapour was removed. This can also be seen from the reproductions in fig. 3, where the green and the two yellow lines are considerably sharper and somewhat narrower in A than they are in B. On the other hand, one cannot help asking why the bands of the new spectrum come out so clearly when those of the Wood spectrum do not. Doubtless the fact that they do would seem to show that these bands have their origin in a system of atomic or molecular vibrations quite distinct from those responsible for the lines of the Wood spectrum. One must remember that that portion of the iodine vapour upon which the light fell was raised to a considerable temperature by the mercury arc, and that it is highly probable, from the facts which have been brought out in connection with the investigation of the high temperature spectrum of

iodine vapour referred to above, that the molecular constitution of the iodine vapour at these higher temperatures is in all probability different from what it is at ordinary room temperatures. It might, therefore, happen that the molecules of the heated iodine vapour would not be stimulated to emission at all by the light from the green and the yellow lines of the mercury arc spectrum. If this were so, the lines in the Wood spectrum could not then appear on the plates. At the same time, it might be possible that the molecules of the heated vapour would respond to a stimulation by the light from a line or lines in the ultra-violet portion of the mercury arc spectrum. If such a stimulation had the effect of causing the heated vapour to emit a fluorescence spectrum, the light constituting this spectrum might easily pass through the cold vapour without any absorption and so give rise to the bands obtained in the present investigation.

In conclusion, I wish to acknowledge the services of my assistants, F. Mezen and P. Blackman, the one in quartz-blowing and the other in preliminary work on the photographs.

The Abnormal Kinetic Energy of an Ion in a Gas.

By F. B. Pidduck, M.A., Fellow of Queen's College, Oxford.

(Communicated by Prof. J. S. Townsend, F.R.S. Received and read March 13, 1913.)

1. In a paper on "The Charges on Ions in Gases, and the Effect of Water Vapour on the Motion of Negative Ions," Townsend* showed that when a stream of ions is moving in an electric field the extent to which it spreads out as it advances depends on the dryness of the gas as well as on the electric force, indicating that the rate of diffusion in dry air is abnormally great in comparison with the velocity under an electric force. It was suggested (*loc. cit.*, p. 469) that this could be explained on the supposition that the ions were not in "thermal equilibrium" with the molecules of the gas, but that their mean kinetic energy exceeded that of an equal number of gas molecules in the ratio k to unity, where k depends on the pressure and the electric force. Townsend mentioned a possible means by which this abnormal energy might arise, namely, that the extra velocity acquired by an ion in an interval

* J. S. Townsend, 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 464.

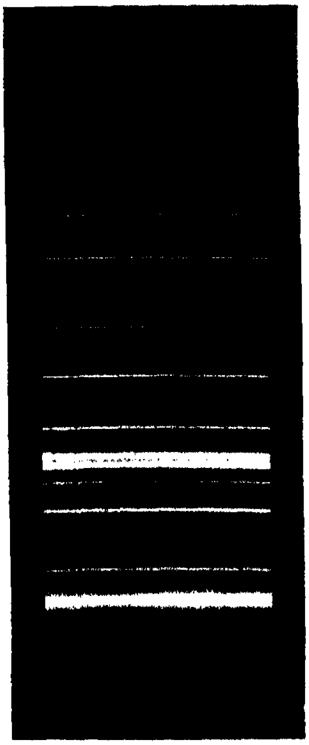


Fig. 1.

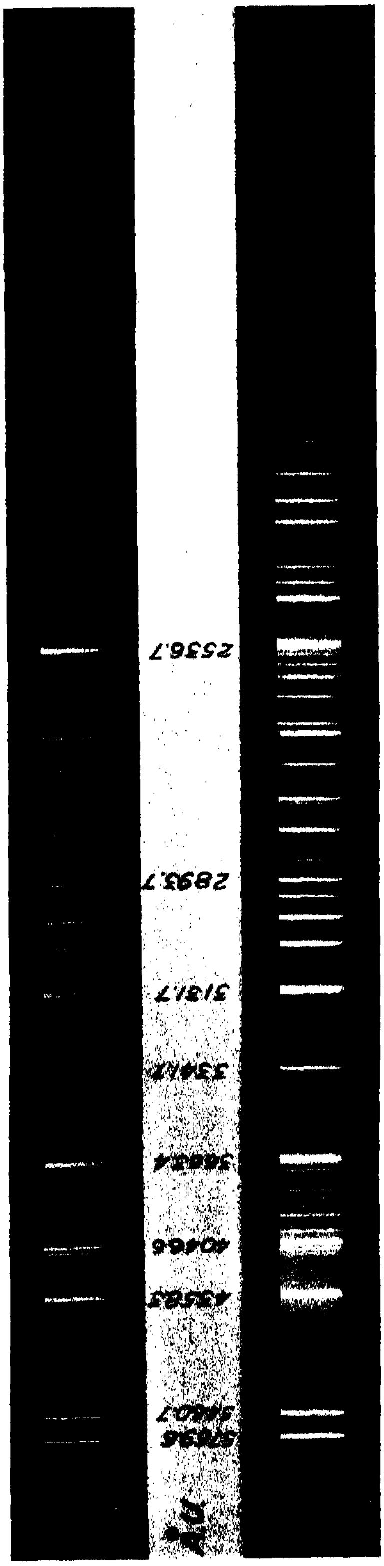
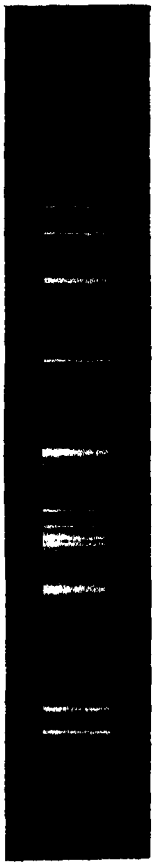


Fig. 3.



between collisions was not all lost by collision with a gas molecule, so that energy might accumulate for some time. The effect has been further studied by Haselfoot,* both observers showing that k is, at any rate approximately, a function of X/p only, where X is the electric force and p the pressure of the gas.

It seemed to the author that it would be desirable to investigate the matter quantitatively on the basis of the kinetic theory of gases, since we are here dealing with the validity or non-validity of the law of equipartition of energy. It is shown in this paper that it is easy enough to obtain theoretical support for the assumption of abnormal kinetic energy; in fact, the values of k predicted by pure theory are considerably in excess of those actually observed. In order to prevent misunderstanding, it may be stated that the law of equipartition of energy in the kinetic theory is only proved to be true when the molecules are left to themselves in the absence of external forces.

2. The most satisfactory way of treating these questions is that developed by Maxwell† in his later papers, and carried out by him on the assumption of an inverse fifth-power law of repulsion between molecules. Where not otherwise stated we shall follow the notation used by Jeans‡ in his account of Maxwell's theory.

Let n = Number of ions per cubic centimetre of the gas, small in comparison with

N = Number of molecules of gas per cubic centimetre.

(X, Y, Z) = Electric force.

θ = Absolute temperature of the gas.

(u, v, w) = Velocity of an ion.

$(u_0, v_0, w_0) = (\bar{u}, \bar{v}, \bar{w})$, the mass-velocity of a group of ions. Writing $(u, v, w) = (u_0+U, v_0+V, w_0+W)$, (U, V, W) is called the velocity of agitation of an ion, so that $\bar{U} = \bar{V} = \bar{W} = 0$.

(u', v', w') = Velocity of agitation of a gas molecule.

m, M = Mass of ion and molecule respectively.

$\alpha\theta$ = Average kinetic energy of agitation of a gas molecule.

$k\alpha\theta = \frac{1}{2}m(\overline{U^2}+\overline{V^2}+\overline{W^2})$ = average kinetic energy of agitation of the ions in a specified small region.

$$h = 3/4\alpha\theta, \quad \lambda = MNK^{\frac{1}{2}}(m+M)^{-\frac{1}{2}}, \quad T = (m+M)^{\frac{1}{2}}/MNA_1K^{\frac{1}{2}}.$$

* C. E. Haselfoot, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 350.

† J. C. Maxwell, 'Phil. Trans,' vol. 157; 'Collected Papers,' vol. 2, p. 26.

‡ 'Dynamical Theory of Gases,' Chap. XV.

Then Maxwell's general equation of transfer* becomes, in the case of steady motion,

$$\frac{\partial}{\partial x}(n\overline{uQ})+\frac{\partial}{\partial y}(n\overline{vQ})+\frac{\partial}{\partial z}(n\overline{wQ}) = \frac{ne}{m}\left[X\left(\overline{\frac{\partial Q}{\partial u}}\right)+Y\left(\overline{\frac{\partial Q}{\partial v}}\right)+Z\left(\overline{\frac{\partial Q}{\partial w}}\right)\right]+\Delta Q. \quad (1)$$

The equation of continuity is

$$\frac{\partial}{\partial x}(nu_0)+\frac{\partial}{\partial y}(nv_0)+\frac{\partial}{\partial z}(nw_0) = 0. \quad (2)$$

Putting $Q = u, v, w$ in succession gives the three well-known equations of the type

$$\frac{\partial}{\partial x}(n\overline{u^2})+\frac{\partial}{\partial y}(n\overline{uv})+\frac{\partial}{\partial z}(n\overline{uw}) = \frac{neX}{m}+\Delta u. \quad (3)$$

Putting $Q = u^2$, we have

$$\frac{\partial}{\partial x}(n\overline{u^3})+\frac{\partial}{\partial y}(n\overline{u^2v})+\frac{\partial}{\partial z}(n\overline{u^2w}) = \frac{2neXu_0}{m}+\Delta u^2, \quad (4)$$

and, similarly,

$$\frac{\partial}{\partial x}(n\overline{u^2v})+\frac{\partial}{\partial y}(n\overline{uv^2})+\frac{\partial}{\partial z}(n\overline{uvw}) = \frac{ne}{m}(Xv_0+Yu_0)+\Delta uv. \quad (5)$$

The quantities denoted by ΔQ, which represent the effect of collisions on Q, are calculated by Maxwell,† the assumption of the inverse fifth-power law now entering for the first time. In the present notation the results are

$$\Delta u = -nu_0/T, \quad (6)$$

$$\Delta u^2 = -\lambda n\left\{2A_1(m\overline{u^2}-\tfrac{2}{3}\alpha\theta)+A_2M(2\overline{u^2}-\overline{v^2}-\overline{w^2})\right\}, \quad (7)$$

$$\Delta uv = -\lambda n(2A_1m+3A_2M)\overline{uv}. \quad (8)$$

3. The immediate problem with which we are concerned is to find the kinetic energy in a stream of ions advancing in a fixed direction, for example the axis of x, the motion depending on the co-ordinate x alone. Then

$$nu_0 = \text{constant}, \quad (9)$$

$$d(mn\overline{u^2})/dx = neX-mnu_0/T, \quad (10)$$

$$d(mn\overline{u^3})/dx = 2neXu_0-\lambda mn\left\{(2A_1m+3A_2M)\overline{U^2}-\tfrac{4}{3}A_1\alpha\theta-2A_2Mk\alpha\theta/m +(2A_1m+2A_2M)u_0^2\right\}, \quad (11)$$

$$d(mn\overline{uv^2})/dx = -\lambda mn\left\{(2A_1m+3A_2M)\overline{V^2}-\tfrac{4}{3}A_1\alpha\theta-2A_2Mk\alpha\theta/m -A_2Mu_0^2\right\}, \quad (12)$$

$$d(mn\overline{uw^2})/dx = -\lambda mn\left\{(2A_1m+3A_2M)\overline{W^2}-\tfrac{4}{3}A_1\alpha\theta-2A_2Mk\alpha\theta/m -A_2Mu_0^2\right\}. \quad (13)$$

* Jeans, p. 277.

† 'Collected Papers,' vol. 2, pp. 47–48.

Here k may be a function of x, and the equations will apply to the motion of a stream of ions advancing with gradual rise of kinetic energy. It is natural to inquire whether there is any final state towards which the motion tends when the stream has travelled some distance. In this case the d/dx terms vanish, and (10) gives

$$u_0 = e\mathrm{XT}/m. \tag{14}$$

Substituting for X from this equation in (11), (12), and (13), we find

$$\left.\begin{aligned}(2\mathrm{A}_1 m + 3\mathrm{A}_2\mathrm{M})\overline{\mathrm{U}^2} &= \tfrac{4}{3}\mathrm{A}_1\alpha\theta + 2\mathrm{A}_2\mathrm{M}k\alpha\theta/m + 2(\mathrm{A}_1-\mathrm{A}_2)\mathrm{M}u_0^2,\\ (2\mathrm{A}_1 m + 3\mathrm{A}_2\mathrm{M})\overline{\mathrm{V}^2} = (2\mathrm{A}_1 m + 3\mathrm{A}_2\mathrm{M})\overline{\mathrm{W}^2} &= \tfrac{4}{3}\mathrm{A}_1\alpha\theta + 2\mathrm{A}_2\mathrm{M}k\alpha\theta/m + \mathrm{A}_2\mathrm{M}u_0^2.\end{aligned}\right\} \tag{15}$$

These latter equations yield on addition

$$k-1 = \mathrm{M}u_0^2/2\alpha\theta\,; \tag{16}$$

or, if Ω is the "root-mean-square value" of the velocity of agitation of the gas molecules,

$$k-1 = u_0^2/\Omega^2. \tag{17}$$

4. The inverse fifth power law has the advantage of allowing a perfectly rigorous solution of the present problem, free from all considerations of approximation. As, however, the formula (17) is not in agreement with experiment it is desirable to consider another law of force, namely, that both ion and molecule are elastic spheres. Some useful information is given by equations (15) as to the distribution of velocities of agitation in various directions. In general $\overline{\mathrm{U}^2}$, $\overline{\mathrm{V}^2}$, and $\overline{\mathrm{W}^2}$ are unequal, and their differences are of the order of magnitude of u_0^2. In two cases, however, the differences are small in comparison with the absolute value of any of the quantities; namely, when k is nearly unity, and when m is small in comparison with M. We shall, therefore, not be far wrong in assuming Maxwell's law of distribution as a first approximation.

Let $f_1(\mathrm{U}, \mathrm{V}, \mathrm{W})\,d\mathrm{U}\,d\mathrm{V}\,d\mathrm{W}$ represent the fraction of the whole number of ions which have velocities of agitation in the range $(\mathrm{U}, \mathrm{V}, \mathrm{W})$ and $(\mathrm{U}+d\mathrm{U}, \mathrm{V}+d\mathrm{V}, \mathrm{W}+d\mathrm{W})$: then Maxwell's law is expressed by

$$f_1 = (hm/k\pi)^{3/2}e^{-hm(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)/k}. \tag{18}$$

There is no doubt as to the corresponding function $f_2(u', v', w')$ for the molecules of the gas, namely,

$$f_2 = (h\mathrm{M}/\pi)^{3/2}\,e^{-h\mathrm{M}(u'^2+v'^2+w'^2)}.$$

We shall suppose for the sake of generality that the collision of ion and molecule is not perfectly elastic, an assumption which allows roughly for a possible loss of energy on collision, though it renders the validity of (18) more doubtful than it might otherwise be. Under these conditions

the calculation of ΔQ is reduced to that of certain multiple integrals.* Neglecting terms in u_0^2 as a first approximation, and taking m as small in comparison with M, we find

$$\Delta u = -\tfrac{8}{3} n \mathrm{N} \sigma^2 u_0 f (\pi k / h m)^{\frac{1}{2}},$$

where σ is the molecular radius, and f stands for $\frac{1}{2}(1+e)$, e being the coefficient of restitution. Hence

$$u_0 = \frac{3eX}{16 \mathrm{N} \sigma^2 f} \left(\frac{3}{\pi m k \alpha \theta} \right)^{\frac{1}{2}}, \tag{19}$$

a result which for $f = k = 1$ agrees with one found by Langevin.†

In determining $k-1$, which is of the nature of a second order approximation, we have to consider the correction to be applied to the Maxwellian formula (18). It would be exceedingly difficult to determine the form of the function f_1 with rigour, although Boltzmann‡ has given an equation satisfied by it; hence it is most natural to assume a formula of the type

$$f_1 = (p + q\mathrm{U}^2)\, e^{-\nu(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}, \tag{20}$$

in which q is a small quantity of the order u_0^2. Its presence enables us to satisfy the equation $\Delta v^2 = 0$, which would remain unsatisfied on a pure Maxwellian law. We approximate to the second order in u_0 and eliminate q from the equations $\Delta u^2 = -2ne\mathrm{X}u_0/m$ and $\Delta v^2 = 0$, afterwards replacing p by $(hm/k\pi)^{3/2}$ and ν by hm/k. A somewhat tedious calculation on these lines yields the result

$$k - f + \frac{k\mathrm{M}}{m}(1-f) = \frac{u_0^2}{\Omega^2} \frac{4f-3}{2-f}. \tag{21}$$

In this formula we have neglected m in comparison with M, except in the important term $k\mathrm{M}(1-f)/m$. When the collision is perfectly elastic $f = 1$ and

$$k - 1 = u_0^2/\Omega^2,$$

exactly as in equation (17).

5. We have now to consider the equations (17) and (21) in the light of recent experiments.§ Taking $\Omega^2 = 2{\cdot}5 \times 10^9$ for air at 15° C., the following table gives the kind of results obtained.

* *Cf.* Jeans, 'Dynamical Theory of Gases,' equation (685), p. 289.

† P. Langevin, 'Ann. Chim. Phys.,' 1905, Ser. 8, vol. 5, p. 245; e, of course, here denotes the charge on the electron.

‡ Boltzmann, 'Gastheorie,' vol. 1, p. 114 (contains some obvious misprints).

§ J. S. Townsend and H. T. Tizard, 'Roy. Soc. Proc.,' 1913, A; also C. E. Haselfoot, *loc. cit.*

X/p	0·2	0·5	1	2	5	10	20	50	100	150
$u_0/10^5$	5	9	12·5	17·5	30	52	90	173	270	350
$k-1$ (observed)	1·8	4·5	9	20	35	44	55	100	160	210
$k-1$ from (17)	100	320	630	1200	3600	$1·1 \times 10^4$	$3·2 \times 10^4$	$1·2 \times 10^5$	$2·9 \times 10^5$	$4·9 \times 10^5$

The theoretical values are thus much too high throughout, particularly at the larger electric forces.

The source of the discrepancy might be sought in the remark that the final state here contemplated was not attained in the experiments of Townsend and Tizard; but though there is some theoretical support for this view it would lead to the conclusion that the observed values of k are not functions of X/p only, and is thus negatived by experiment. The equation (21), however, taken in a wide enough sense, is capable of explaining the discrepancy. If f is less than unity there is a loss of energy on impact, and it appears reasonable to suppose that this loss will increase as more and more ions reach the velocity necessary to form other ions by collision. In fact, we calculate the quantity f as a function of X/p by means of equation (21), using the observed values of u_0 and k. Since M/m has the value $5·3 \times 10^4$, a very slight defect of f from unity will cause a great drop in the value of k, while leaving the formula (19) for the mobility practically unaltered. The coefficient of restitution e, here viewed in a somewhat wider sense, may be called the energy coefficient; and we may say roughly that the loss of energy on collision under a given electric force is on the average that of an imperfectly elastic impact with the corresponding value of e. The results of the calculation are:—

X/p......	0·2	0·5	1	2	5	10	20	50	100	150
Energy coefficient e	0·9986	0·9976	0·9975	0·9976	0·996	0·99	0·98	0·95	0·93	0·92

The formula (21) cannot be pushed to extremes. It is clearly erroneous when f is less than $\frac{3}{4}$, *i.e.* when e is less than $\frac{1}{2}$; but the formula (20) becomes less and less applicable at high speeds, and would probably fail before e sank to this value. As, however, (21) reduces to the exact formula (17) when $f = 1$ it may be regarded as a reasonable generalisation to cover the case of loss of energy by collision.

It is of interest to calculate the ratio of the velocity of drift u_0 to the

velocity of agitation ω of the ions themselves. Since $m\omega^2 = k\mathrm{M}\Omega^2$ we have from (21)

$$\frac{u_0^2}{\omega^2} = \frac{2-f}{4f-3}\left[\frac{m}{\mathrm{M}}\frac{k-f}{k}+1-f\right]. \tag{22}$$

From the preceding numbers it is clear that u_0/ω is quite small for low values of X/p; but the ratio rises with increasing electric force, and ultimately becomes comparable with unity.* It may, of course, happen that there is no steady state of uniform velocity in this case.

The equation (17), though it gives values of k that are too high, applies to the case of an ion whose mass may have any ratio to that of the gas molecule. If m is comparable with M, ω is comparable with Ω. Hence unless k is very near to unity u_0 is of the order of magnitude of ω. Thus with positive ions, the mass of which is comparable with that of a molecule, we should expect the velocity of drift of the ions to approach their velocity of agitation for electric forces less than those required to produce abnormal kinetic energy. Much higher electric forces would be required, but the equation of diffusion would be seriously invalidated, and the effects observed by Townsend greatly modified. It thus appears probable that these effects are limited to negative ions.

* If $f=1$, $u_0^2/\omega^2 < m/\mathrm{M}$ for all values of k.

The Influence of Chemical Constitution upon Interfacial Tension.

By W. B. Hardy, F.R.S.

(Received October 19, 1912,—Read January 16,—Revised March 11, 1913.)

If T_B be the pull per linear centimetre exerted by the surface tension of a pure fluid B, then, if the surface be increased by 1 sq. cm., the increase in surface energy is also T_B. Let a thin film of a second fluid A immiscible with B spread over the surface of B; the tension of the composite surface so formed is less than that of pure B, otherwise spreading would not occur. When the film of A has become sufficiently thick two independent surfaces are formed, one of pure A, the other the interface between A and B. Denoting these respectively by T_A and T_{AB} the energy of the two for each unit of the original surface of pure B is

$$T = T_A + T_{AB}, \qquad (1)$$

and this quantity T is not affected by further addition of A. Therefore in the spreading of A upon B we have, as the limits of the change of surface energy, $T = B$ and $T = T_A + T_{AB}$.

In an earlier paper* I gave reasons for believing that the changes in the value of T between these limits depend mainly upon the chemical constitution of A.

Between the limits $T = T_B$ and $T = T_A + T_{AB}$, lies a series of values of T when A is not present in mass. The phenomena over this region are complex, therefore, in order to obtain a simpler presentation of the influence of chemical constitution it is necessary to have A as well as B present in mass. The equation then reduces to the simple form $T = T_{AB}$. It is with measurements of the quantity T_{AB} that we are concerned in this paper.

Following Dupré† we may write

$$T_{AB} = T_A + T_B - 2T'_{AB}, \qquad (2)$$

in which $2T'_{AB}$ is the work done per unit of area of interface by the attraction of A for B when a surface of A is allowed to approach normally and touch a surface of B. Since the quantity $2T'_{AB}$ is the total work expended in forming unit area of interface by the molecular forces which operate between A and B it follows that evidence of the influence of chemical constitution upon surface energy must be looked for in a comparison of this quantity when different fluids A form an interface with a constant fluid B—

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 610.

† 'Théorie Mécanique d. l. Chaleur,' Paris, 1869, p. 369. See also Lord Rayleigh, 'Phil. Mag.,' 1890, [5], vol. 30, p. 461.

in this case water. The tension T_{AB} will not serve our purpose so well since it depends directly upon the tension of A itself.

The first person to introduce the critical constants into considerations of surface energy was Eötvös,* and he was followed by Ramsay and Shields.† The argument may be stated as follows:—

In the gas equation $pv = R\theta$, if v be kept constant p decreases with fall of θ until where $p = 0$, $\theta = -273$ or absolute zero; the origin of the scale of temperature is thus also the origin of the scale of pressure. The absolute zero of surface energy is the critical temperature, and if an equation analogous to the gas equation be used, namely $Ta = K\tau$, in which a is the area of surface, the temperature τ must be measured in centigrade degrees downwards, the critical temperature being taken as zero. Corresponding to this equation the relation between tension and temperature should be a linear one—a relation proved experimentally by Ramsay and Shields. Near the critical point, however, the linear relation is departed from, with the result that the line which represents the relation between Ta and τ cuts the axis of temperature at a point some degrees below the critical point. The equation for the linear portion of the curve, that is for temperatures other than those near to the critical temperature, is therefore

$$Ta = K(\tau - d).$$

In comparing different substances that surface must be taken which is formed by the same number of molecules. Such a surface, as Eötvös pointed out, is the side of the cube which contains 1 gramme molecule. If v be the volume of a gramme molecule in cubic centimetres, that is the molecular volume, the area of the side of the cube will be $v^{2/3}$. Call this a molecular surface. The equation now becomes

$$Tv^{2/3} = K(\tau - d). \tag{3}$$

This equation enables us to calculate the constant for the pure fluid A from measurements of T_A and T_{AB}.

Putting $(\tau - d) = 1$ in equation (3) we see that K is the gain in molecular surface energy per degree of temperature. An equation precisely similar to (3) for an interface would have as its zero of temperature, not the critical points of the pure fluids A and B, but the temperature at which A and B become completely miscible. This temperature is unknown for the pairs of substances used; an equation for the interface may, however, be derived from equations (2) and (3), namely

$$K_A = \frac{(T_{AB} + 2T'_{AB})\,v_A^{2/3} v_B^{2/3} - K_B(\tau_B - d)\,v_A^{2/3}}{(\tau_A - d)\,v_B^{2/3}}. \tag{4}$$

* 'Wied. Annal.,' vol. 27, p. 452.

† 'Phil. Trans.,' 1893, A, p. 647.

This equation enables us to calculate the constant for the pure fluid A from measurements of T_A and T_{AB}.

Experimental Methods.—These need somewhat detailed discussion. The surface tensions were measured by determining the weight of the drops of liquid delivered by certain capillary tubes, of which No. 1 was straight and No. 2 bent at right angles. The procedure may best be described by a random selection of an experiment.

Pure oleic acid was poured over some distilled water in a cylindrical vessel until it formed a layer about 3 cm. deep. The straight tube (No. 1), previously cleansed with sulphuric and chromic acids and washed out with distilled water, was dipped into the lower layer (distilled water) and enough fluid drawn up. The point of the tube being raised so as to be in the upper layer, the contents were allowed slowly to form drops which were counted while 3·56 c.c. of fluid left the tube. The operation was repeated with this result:—

Temperature, 20°. Tube 1. Capacity, 3·56 c.c.; number of drops, 44, 44·5, 43·8, 43·8.

Tube 2, bent at right angles, was next filled with the upper layer (oleic acid) and drops allowed to form and float up when the point was immersed in the lower layer (water).

Tube 2; capacity, 1·517 c.c. No. of drops, 37·1 : 37·2.

Tube 1 was then cleaned, dried, filled with oleic acid at 20° and a series of 10 drops allowed to fall into a weighed stoppered weighing bottle.

Weight of 10 drops, 0·1625, 0·1647, 0·1617, 0·1617. Mean, 0·1626.

Loss of weight by evaporation, determined by control experiment, 0·0000.

From these data we now have to calculate the quantities T_{AB} and T_A. The formula frequently used to compute the surface tension from the weight of a drop delivered by a tube is $T = mg/2\pi r$, when m is the weight of the drop and r the radius of the tube; but this formula gives little more than half the true surface tension. The weight of the drop cannot be calculated from statical consideration: the detachment of the drop is a dynamical effect. A complete solution of the dynamical problem is impracticable. It was attempted by Dupré* and the argument has been restated by Lord Rayleigh,† who found the formula $T = mg/3{\cdot}8r$ to be a close approximation for thin-walled tubes.

The tubes used by myself had the following dimensions at the orifice:—

No. 1.	External radius, 0·1165 cm.	Internal radius, 0·0615 cm.
No. 2.	„ „ 0·0917 „	„ „ 0·0629 „

* *Loc. cit.*, p. 327.

† 'Phil. Mag.,' 1899, [5], vol. 48, p. 321.

For these tubes the factor 3·8 was found too low. It applies apparently only to tubes of larger radius. This is at once seen when the tension of water is calculated from the weight of the drop delivered by tubes used by Lord Rayleigh.* The first six on his table give the following values:—

15°.		
r.	m.	T (factor 3·8).
cm.	grm.	
0·11175	0·0375	86·7
0·17017	0·0526	79·72
0·24256	0·0712	75·7
0·254	0·0755	76·7
0·32512	0·0923	73·2

For the smaller tubes therefore the tension comes out too high, the value for water at 15° being 74·45. I therefore determined experimentally the factor for water for tube 1 and found it 4·413 at 16° and 4·391 at 18·5°, and these values were used in computing my results. With Lord Rayleigh's values I now get for his smallest tube:—

15°. r, 0·11175; m, 0·0375; factor, 4·413; T, 74·64;

which agrees closely with the standard value 74·45.

For the quantity T_{AB} we have for the weight of the drop, if v be the volume of fluid delivered, n the number of drops and D_A the density of the upper layer, D_B that of the water: $m = v(D_B - D_A)g/n$ and the formula becomes

$$T_{AB} = \frac{v(D_B - D_A)g}{nrF}.$$

Returning to the actual experiment, when the lower layer forms drops in the upper layer since water wets the glass of the capillary tube they detach themselves from the whole face of the end of the tube, therefore r is here the external radius or $r = 0·1165$ cm. But when oleic acid is delivered into water by tube 2 it does not wet the walls and the drops are detached from the lumen, and r is the internal radius or 0·0629 cm. When oleic acid is delivered from tube 1 in air, however, it wets the walls and the external radius must be used.

We therefore have:—

Tube 1. Mean number of drops, 44, r, 0·1165; T_{AB}, 15·66 ⎫ Mean, 15·15.
Tube 2. „ „ 37·15 r, 0·0629; T_{AB}, 14·64 ⎭

Tube 1. Weight of one drop of oleic acid in air, 0·1626; T_A, 31·15.

* *Loc. cit.*, p. 324.

T_B, the tension of water at 20°, being 73·70, we get from equation (2)

$$T'_{AB} = 44{\cdot}85.$$

Inspection of Table III shows that the values of T_{AB} obtained for different substances with water sometimes agree closely for the two tubes, sometimes differ widely. How far may the means be trusted to give the true value? The best evidence that they do so is to be found in the consistent way in which the quantity T'_{AB} follows chemical constitution. The chief error arises from viscosity, for with very viscous fluids the drop takes an appreciable time to break away, therefore if the column of fluid in the capillary tube be moving with any velocity *at the time of breaking* the drop is over filled and the tension comes out too high. As an extreme case take the very viscid ricinolic acid at 16°, just above the temperature of solidification. When each drop occupied about 40 seconds in forming and breaking away the numbers were—Tube 1, 20·1, 20, 19·8. But when the time was reduced from 40 to 10 seconds the number fell to 8. Now with respect to this source of error the conditions are entirely dissimilar in the two tubes, in tube 1 a drop attached over the whole face is being filled by a stream of relatively small section, while in tube 2 the whole column of fluid which supports the drop is in movement. The concordance of the means leads one to conclude that in the first case the kinetic energy leads to over-inflation of a drop, while in the second case it causes the drop to break away too soon and therefore to be too small. Lord Rayleigh says that "sufficient time must be allowed for the normal formation of the drop," but the most important condition to observe is that the movement of the column of fluid in the tube should be as near as possible zero at the moment when the drop breaks away.

Where the critical constants are known the accuracy of the results may be tested by equations (3) and (4). Ramsay and Shields find that $K = 2{\cdot}21$. I get the following, putting $d = 6$ as they do.

Table I.

	T_A.	$v^{2/3}$.	$t°$.	$(\tau - d)$.	K_A.
Carbon bisulphide	30·88	15·396	17	252	1·80
Carbon tetrachloride	24·51	20·999	17	260	1·98
Benzene	27·59	19·624	20·5	261·5	2·07
Toluene	26·82	22·154	22	292·5	2·03
Octylene	21·07	28·87	17·2	275·6	2·20
Cyclohexane	24·21	22·78	16·8	257	2·14
Ethyl-benzene	27·68	24·56	17·5	322·4	2·12
Octane	20·63	29·70	18·5	272	2·25

Rejecting the value for carbon bisulphide as being clearly too low, the order of agreement is the same as that found for various substances by Ramsay and Shields, and the mean is 2·11. Similarly from equation (4) we may calculate the constant K_A, using the interfacial tension T_{AB} as one of the data. The constant K_B, since the molecules of water associate in the fluid state to some multiple of the chemical molecule, is less than 2·11. The standard on which all measurements in this paper are based is $T_B = 74$ at 18°. Taking 365° as the critical temperature of water, equation (3) gives $K_B = 1·49$. Equation (4) now gives the following values for K_A:—

Table II.

Carbon bisulphide	1·88	Octylene	2·17
Carbon tetrachloride	1·98	Cyclohexane	2·16
Benzene	2·10	Ethylbenzene	2·12
Toluene	2·04	Octane	2·25

Here again the agreement justifies the conclusion that the mean value of T_{AB} is not far removed from the actual value. The most serious source of error, especially in the case of substances which have little power of lowering the tension of water, lies in the presence of more active impurities. Rigorous circumspection is necessary both in the handling of the water, and of the other fluids, and in their preparation. The effect of a trace of impurity is hardly to be credited. Cyclohexane, a saturated hydrocarbon, does not spread upon water. In some of it 0·00015 per cent. by weight of oleic acid was dissolved, making a 0·0004 normal solution. The fluid now flashed over a water surface and the tension of the interface with water was found to have fallen from 55·15, that of pure cyclohexane-water, to 32·37. It cannot be without interest to notice that the concentration of oleic acid employed is of the order of concentration needed in the case of such physiologically active substances as adrenalin reckoned as percentage of the body weight of the animal; also, if FitzGerald's view be true that the force of contraction of a muscle is derived from changes in the tension of internal surfaces, such a concentration of a similarly active body would reduce the absolute force by about 50 per cent. While dealing with the question of chemical purity certain special cases must be mentioned.

A sample of octane purchased from Kahlbaum gave the following values, T_{AB} 29·3, T'_{AB} 32·6. As these differed widely from the values obtained for other saturated bodies the sample was freed from unsaturated substances, by shaking for four weeks with many changes of concentrated sulphuric acid. It was then washed with water and distilled from metallic sodium, and the fraction which came over at 123–126° now gave the values

T_{AB} 53·48 and T'_{AB} 20·54, which accord with the values found for other saturated bodies.

Octylene, as obtained from Kahlbaum, gave T_{AB} 12·9, T'_{AB} 41. It was then distilled and a fraction of B.P. 122—124° collected, giving the values T_{AB} 22·48, T'_{AB} 36·24. Like octane it was found to be impossible to get a fraction giving a perfectly constant boiling point. A series of fractionations was therefore undertaken and two fractions collected, (A) 120—122°, (B) 122—124°, Bar. 758. The B.P. of octylene is given in Beilstem as 122—123°, and as 124·6° at 796·6 mm. Fraction A gave T_{AB} 22·61, T'_{AB} 36·18. Fraction B, T_{AB} 23·06, T'_{AB} 35·95.

The mean of these values is the best that can be got for octylene by fractional distillation.

The substances employed were for the most part purchased from Kahlbaum and, when possible, distilled to a constant boiling point just before use. Some specimens were lent to me by Dr. Ruhemann, to whom I owe also a great debt for his kindness in directly superintending and helping in the purification of each substance. Without the aid which his profound technical knowledge afforded I could not have succeeded in making the measurements.

The effect of any slight degree of mutual solubility of the fluids A and B upon the quantity T_{AB} needs consideration. Let T_a and T_b be respectively the tension of the saturated solution of B in A and of A in B which can form contiguous phases. We then have

$$T_{ab} = T_a + T_b - 2T'_{ab}. \tag{5}$$

Since $T_B > T_A$ in all the cases dealt with, $T_a > T_A$, and $T_b < T_B$, the relation of T'_{ab} to T'_{AB} so far as magnitude is concerned is uncertain, terms of opposite sign being introduced by the presence of A and B on both sides of the interface. When the two solutions are brought into contact the work done is derived from (1) the attraction of A for A and of B for B across the interface, and (2) the attraction of A for B. When pure A and B come into contact (1) is zero, and any degree of miscibility increases the work due to (1) and decreases that due to (2). Therefore, since mutual miscibility introduces effects of opposite signs into the right-hand members of equation (2), the relation of T_{ab} to T_{AB} cannot be predicted.* Whatever the theoretical conclusion practically the value of T_{AB} under the conditions of measurement was found to be sensibly independent of the state of the phases.

* T_{ab} obviously does not include the loss of potential due to the mixing of A and B except at the interface, for, if it did, T_{ab} would be a function of the ratio surface/(mass of A + mass of B).

The alcohol cyclohexanol is soluble in 28 parts of water. Dry cyclohexanol on water gave the following values:—

16·2°. Density alcohol, 0·948, water = 1.

T_{AB}. Tube 1, 3·951; Tube 2, 3·665. Mean, 3·808.

The layers were then thoroughly shaken together in a stoppered vessel and left 24 hours. For the layers mutually saturated I got

16°. Density alcohol layer, 0·9538; density water layer, 0·9986.

T_{AB}. Tube 1, 3·912; Tube 2, 3·693. Mean, 3·802.

Benzene is slightly soluble in water. For two samples I found the following values. Benzene and water not shaken together T_{AB} (17°) 38·01, (20·5°) 36·84; mean 37·42; and after shaking together and leaving for 24 hours, T_{AB} (17°) 37·56, (20·5°) 37·58; mean 37·57.

The experimental results are gathered together in Table III. It will be noticed that whereas the interfacial tension (T_{AB}) only roughly follows the chemical constitution of the fluid A, the quantity T'_{AB} follows it very closely. That is to say, when unit area of a free surface of a fluid is brought into contact with unit area of the free surface of water, the loss of potential, or the work done by molecular forces, is determined by the chemical constitution of the former.

To illustrate this we have the first group of saturated substances, in which I have included oil "C," composed mainly of high boiling-point paraffins. T'_{AB} lies between 20·8 and 24. The introduction of an unsaturated linkage into the paraffin octane raises the value to 36 (octylene). But in the case of a ring compound unsaturated linkages produce a smaller effect, the number rising only to 32·26 (benzene).

The introduction of the OH group into a ring compound increases the quantity by 20 (cyclohexane and cyclohexanol, 51·43 − 21·63 = 19·8); but the effect in the case of the paraffin chain is only about one-half. The presence of the carboxyl group produces the same effect as the OH group, the quantity being increased in the case of capryllic acid by 10·4.

For the esters we have 41 for ethyl hydrocinnamate. The introduction of one more unsaturated linkage increases this only slightly, namely, to the 43 of ethyl cinnamate, and the double ester ethyl phthalate again is only slightly higher, namely, 46. Other relations might be pointed out, but the figures speak for themselves. I prefer to pass on to the more important negative relations.

In the saturated bodies there is a very small but I believe real difference between the paraffin chain and the ring formation, and again between these and the compounds CS_2 and CCl_4. The two cyclic alcohols have practically

Table III.

Substance.	Boiling point.	Temp.	Density (D).	T_A.	T_B.	T_{AB}. I.	T_{AB}. II.	T_{AB}. Mean.	T'_{AB}.	v.	$v^{2/3}$.	$T'_{AB} \times v^{2/3}$.
Octane	123—126°	18·5°	0·7034	20·63	73·93	53·74	52·18	52·96	20·80	161·9	29·7	615
Cyclohexane	Abs. const.	16·8	0·779	24·21	74·2	56·00	54·31	55·15	21·63	108·4	22·73	492
Oil "C"	—	17·0	0·876	30·12	74·15	64·72	57·99	61·35	21·46	—	—	—
Carbon bisulphide	Abs. const.	16·0	1·253	30·88	74·3	58·15	54·15	56·15	24·51	60·42	15·396	377
Carbon tetrachloride	—	17·0	1·63	24·51	74·15	53·2	47·16	50·18	24·24	96·24	20·999	509
Octylene	122—124°	17·0	0·7255	20·82	74·15	22·91	22·07	22·48	36·24	155·18	28·87	1046
Benzene	Abs. const.	20·5	0·879	27·59	73·77	37·68	36·75	37·49	31·93	86·95	19·624	627
Toluene	Abs. const.	22·0	0·8646	26·5	73·40	37·35	34·70	36·02	31·94	104·3	22·154	708
p-Cymene	Abs. const.	13·5	0·8633	27·0	74·57	43·15	41·36	42·25	29·66	155·2	28·87	856
Styrene	144—148°	19·0	0·9028	30·54	73·85	39·70	38·20	38·95	32·72	114·5	23·58	771
Ethyl benzene	Abs const.	17·5	0·879	27·83	74·07	33·93	32·90	33·41	34·24	121·56	24·56	841
Benzene iodide	Abs. const.	16·8	1·831	36·6	74·2	44·88	40·65	42·76	34·00	111·3	23·14	787
Ethyl iodide	Abs. const.	16·0	1·943	26·31	74·3	38·40	37·90	38·15	31·23	80·2	18·59	580
Caprylic acid (n)	Abs. const.	18·1	0·9116	27·3	74·0	8·43	8·35	8·39	46·45	157·9	29·21	1357
Oleic acid	Crystallises	20·0	0·898	30·99	73·70	15·73	14·71	15·22	44·73	314·0	46·19	2066
Ricinolic acid	(Kahlbaum)	16·0	0·9538	34·31	74·3	15·68	14·50	15·09	46·76	312·0	46·73	2185
Cyclohexanol	Abs. const.	16·2	0·9480	32·36	74·3	3·951	3·665	3·808	51·43	105·5	23·77	1223
Octyl alcohol	Abs. const.	17·5	0·8293	26·19	74·07	8·053	7·882	7·967	46·14	156·6	29·04	1340
Benzyl alcohol	Abs. const.	22·5	1·0442	37·93	73·33	4·898	4·891	4·894	53·18	101·6	21·77	1158
Ethyl phthalate	Abs. const.	20·5	1·1175	35·26	73·48	17·10	17·06	17·08	45·83	—	—	—
Ethyl cinnamate	Abs. const.	19·5	1·0497	36·59	73·63	24·01	24·48	24·24	43·00	167·7	30·41	1308
Ethyl hydrocinnamate	Abs. const.	21·5	1·014	33·23	73·48	24·30	24·73	24·5	41·02	175·2	31·31	1284
Castor oil	—	17·0	0·966	35·27	74·15	26·2	19·7	23·0	43·26	—	—	—

v is the volume of one gramme molecule, $v^{2/3}$ the molecular surface.

the same value, and the three fatty acids agree closely. Similarly benzene and the allied substances give values close together. But the remarkable feature of these correspondences is that they are for unit area of interface and not for areas on which equal numbers of molecules impinge.

In the gas equation $Pv = R\theta$ the constant R refers to a volume which contains 1 gramme molecule. Similarly, in the comparison of surface energy, as Eötvös showed (*loc. cit.*), surfaces of the same molecular value must be compared. Such a molecular surface is the face of a cube which holds a gramme molecule of the fluid—or $v^{2/3}$. Tables I and II prove that the values found for T_A and T_{AB} are consistent with this conception of equi-molecular surfaces. But the values for T'_{AB}, though derived from T_A and T_{AB}, are in respect to their relation to chemical constitution independent of the area of the molecular surface. To put the matter in another way—agreement in the values for a particular type of substance, say, saturated compounds, or acids, would by analogy be between the product of the quantities T'_{AB}, which refers to unit area, and the molecular surface ($v^{2/3}$). The last column in Table III shows that this product follows no regular system.

This remarkable fact may be interpreted in various ways, but from whatever aspect it is considered the result is likely to be barren unless molecules are taken account of. If the figures in Table III are interpreted to mean that the energy peculiar to an interface between two fluids is determined by the chemical reaction between the fluids, we may conclude that such action will be complete and independent of the molecular volumes, since the mass of the fluids on either side of the interface is practically infinite. Against this view, however, it is to be noted that chemical action between water and such stable substances as paraffin or cyclohexane, both in mass, is unknown. If it did occur at an interface it could only be as the result of great stresses.

Table III shows most clearly that the quantity T'_{AB} increases with what may be called the chemical reactivity of the fluid B, and especially that it is greatest when the molecules are of the salt type—acids, alcohols, or esters. Such molecules by their constitution readily exhibit electric polarisation, and we have here additional evidence for the fact mentioned in the earlier papers that the chief modifying factor in all interfaces is the development of a contact difference of potential, due to polarisation of the molecules by stresses normal to the interface. If the quantity T'_{AB} represents mainly the specific electric polarisation of the interface, then its value for paraffin, cyclohexane, etc., may represent polarisation due to the water molecules, which are of this salt type. For a surface between two saturated substances not of salt type the quantity might well be zero, in which case we should have

$$T_{AB} = T_A + T_B.$$

From the fact that T'_{AB} is equal for molecules of the same chemical type two conclusions follow. Let each molecule of A attract a molecule of B by a force which is a function only of the distance which separates them, the density term in the Laplacian theory then becomes the reciprocal of the molecular volume and, following the usual notation,

$$T'_{AB} = \frac{\pi}{v_A v_B}\int_0^{\infty} z\psi_{AB}(z)\,dz,$$

v_A, v_B, being respectively the molecular volumes, and z the axis normal to the interface. Then on Young's hypothesis, that molecular attraction is a force which is of constant value over the range a, we have for two similar chemical substances, for which therefore T'_{AB} is the same, $a_1/a_2 = v_A'/v_A''$ That is to say, the range would be proportional to the molecular volume.

The alternative assumption, that the attractive force of a molecule of A for one of B falls off according to some power of the distance which separates them, yields the result that for similar chemical substances, since T'_{AB} is equal, the molecular volumes vary inversely with this power. Thus, if the attractive force $\phi(f)$ be put $= e^{-\beta f}$ then $v_A'/v_A'' = \beta_{\prime\prime}^{5}/\beta_{\prime}^{5}$.

The Tension of Composite Fluid Surfaces.—No. II.

By W. B. Hardy, F.R.S.

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With the figures in Table III of the preceding paper (p. 311) as a guide the problem of the spreading of one fluid over the surface of another may be approached with some sense of security. In an earlier paper* the equation of a composite surface was found to be $T_S = T_A + T_{AB} - Kg$ when T_S is the tension of the composite surface, and Kg a term depending upon gravity. Putting $Kg = 0$, it is seen that spreading will occur only when $T_S > T_A + T_{AB}$, and, at the limit, $T_S = T_B$ that is to the tension of pure water in the experiments under consideration.

Taking $T_B = 74$, the tension of pure water, we have from the last paper

Table I.

	T_A.		T_{AB}.		
Cyclohexane	24·21	+	55·15	=	79·36
Octane	20·63		52·96		73·59
Oil "C"	30·12		61·35		91·47
Carbon disulphide	30·88		56·15		87·03
Carbon tetrachloride	24·51		50·18		74·69

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 610.

That is to say a drop of any of these saturated substances should not spread upon a surface of pure water except octane, and in actual fact none of them do spread, except octane, a drop of which slowly expands on water to form a very thin plate. In the case of all the other substances examined the quantity $(T_A + T_{AB}) < T_B$, and they all flash over a water surface in characteristic fashion.

The word "spreading" here refers strictly to the expansion of a lens of A over a clean surface of B due to the tension of B being greater than the sum of the tensions of the upper and lower surfaces of the lens. The vapour of A will condense on to the surface of B since $T_{AB} < T_B$. At the edge of a lens there is therefore a condensation of vapour of A on to the water, and the sheet of lowered tension so produced is pulled outwards away from the lens by the higher tension of the water surface. The sheet will also be pulled inwards to the lens, a quantity of the vapour of A so finding its way back into the lens. When the saturated substance has a high vapour pressure, such as *e.g.* cyclohexane, the presence of unstable sheets of condensed vapour about each lens is easily detected and readily explains the interesting attractions and repulsions of lenses for each other. When undisturbed a pair of lenses will often continue alternately to attract and repel one another, producing a quite regular pulsation.* The movements cease when the space above the surface is saturated with the vapour of A.

When the vapour tension of A is practically zero a lens shows no trace of spreading of any kind. This is the case with oil "C," which boils somewhere about 400°. For the sum of the tensions of the upper and lower surfaces of a lens of this oil we have $T_A + T_{AB} = 30{\cdot}12 + 61{\cdot}35 = 91{\cdot}47$. It is obviously impossible for the tension of water (74) to pull such a lens out into a sheet.

When the fluid A is a pure chemical substance, or when it is composed of substances having identical influence upon the tension, the phenomena of spreading are always of the simplest. The first added fluid forms a continuous sheet on the surface of the water (B), which may be thickened until spreading ceases, when the excess remains as a single lens. I have met no exception to the rule that, when pure A spreads on water, the equilibrium state is a single lens in tensile balance with a uniform composite sheet of A spread evenly on B. This follows from experiment and also from a consideration of vapour pressures; for let the space above be enclosed, and

* Cantor ('Wied. Annal.,' 1895, vol. 56, p. 492) is wrong in his conclusion that the vapours of fluids which do not "wet" the surface of water will not condense on to the surface. The saturated vapours of the substances mentioned in Table I will condense on to tap water at the same temperature, as a dew of fine lenses, though in the case of carbon bisulphide owing to the high value of $T_A + T_{AB}$ the dew forms only with difficulty.

let a number of lenses of different horizontal diameters be formed. Lenses of greater curvature will lose vapour, and lenses of less curvature will condense it until a single lens is formed. A number of lenses of precisely the same curvature could co-exist, but the equilibrium would probably always be unstable. The condition of equilibrium therefore is twofold, (1) that the lens and the plane surface are in tensile equilibrium according to the equation $T = T_A + T_{AB} - Kg$, and (2) that the vapour tension of the lens and of the plane surface shall be the same.

When a large lens of a fluid whose vapour pressure is negligible is placed on water if it is capable of spreading the lens is at once extended to form an irregular sheet, which then proceeds to contract to one or more lenses which are in tensile equilibrium with a composite surface. Equilibrium is reached quickly when salts are present in the water and slowly when the water is of low conductivity. Taking, for instance, ricinolic acid as an example, equilibrium is reached with tap water in 20 seconds, and with distilled water only after perhaps 20 minutes. When distilled water is used there appears to be a large tangential viscosity which impedes contraction of the excess oil. As I have already pointed out* the film is at a different electrical potential to the underlying water, and the tangential viscosity may be due to the low conductivity of distilled water delaying the dissipation of electrical energy. Whatever be the true explanation the contrast is remarkable. When distilled water is used the tangential viscosity is so great as to allow the sheet of acid to develop wrinkles and folds as though it were a solid.

What we may picture as happening in all cases is that since $T_B > T_A + T_{AB}$ the lens is at once pulled out to form a sheet. From the visible edge of the sheet fluid is spreading on to the surface of B, at first rapidly, then more slowly, the flow being impeded by the viscosity of the film and possibly by other causes. As a consequence of this streaming from the edge the tension of the plane composite surface falls, and as it does so the extended lens contracts. The sheet formed by the first rapid extension of the lens of A frequently is unstable and ruptures. Circular spaces appear which are occupied by a composite surface similar to the composite surface outside the lens. The chief features on which I would insist here are (1) the relatively gradual formation of the composite surface by increase in the mass of A per unit area until it is in tensile equilibrium with a convex lens of A, and (2) the fact that when a lens of A is extended to form a sheet, the sheet is unstable if its thickness fall below a certain quantity.

When the fluid A has a sensible vapour tension—such as benzene or

* 'Roy. Soc. Proc.,' 1911, B, vol. 84, p. 220; also 1912, A, vol. 86, p. 608.

toluene—other features appear. Let us start with excess benzene placed on water, and exposed to air, the benzene is pulled out into an irregular sheet. When the air space is covered in so that it may become saturated with benzene vapour the sheet contracts to one or more lenses which are highly convex and quite immobile. These lenses are in tensile equilibrium with a composite surface of benzene and water. If the cover to the space be removed benzene evaporates from the composite surface, the tension rises, and the convex lens (or lenses) is at once pulled out to a sheet. It is very easy again to notice that an over extended sheet of benzene is unstable and ruptures. It will be noticed that whatever the vapour tension of A, whether it be high or insensible, the system settles down to the same state, namely, a composite sheet in tensile equilibrium with a convex lens of A. Now the tension of one face of the lens is T_{AB}, and of the other is T_A, or if B be soluble in A some quantity slightly greater than T_A. Therefore, since the lenses are convex we have for the equilibrium state the important relation $T_B < T_A + T_{AB}$.

In the case of the chemically saturated substances in Table I the lens is not pulled out to form a sheet, and fluid cannot be drawn from its edge on to the surface of the water since $T_A + T_{AB} > T_B$. But the vapour condenses on to the water since $T_{AB} < T_B$. This may readily be proved by pouring the vapour of octane, or carbon bisulphide, etc., on to a clean surface of water and noticing the movement of lycopodium grains dusted on to the surface.

When A is not a pure substance but a mixture of substances which individually produce effects of different magnitude upon the tension of B, the phenomena of spreading are more complex. Mixtures of *e.g.* cyclohexane or oil "C" and oleic acid or stearic acid at first flash over the surface as a continuous sheet which, viewed at certain angles, is uniformly and brilliantly coloured. From the particular colour we may put this sheet as from 300 to $1000\mu\mu$ thick. The sheet is unstable and ruptures, circular spaces appearing. As these spaces extend a horizontal net is formed, and finally the bars of the net rupture and the isolated masses contract to lenses. The total time occupied in forming the lenses, and the relative duration of particular stages depend upon the ratio of the components of A, upon their nature, and upon the concentration of electrolytes in the water. Increasing the number of components as a rule lengthens the total time and the complexity of the phenomena, and the vivid play of Newtonian colours is then very beautiful. By increasing the number of components a composite sheet may be formed of films of different thicknesses which pass abruptly into each other. The whole surface shows sharply determined coloured areas, red, blue, green, bronze, etc., which endure for days.

The phenomena ultimately depend upon the accumulation by diffusion of the most active constituents at the interface, and their complexity and durability are due to the slowness with which tangential diffusion can occur owing to the small depth of the film. The phenomena, occurring as they do on the surface of water, may be said to take place in two dimensions. If they occupied the mass of the fluid, that is to say, if they were in three dimensions, the unstable sponges, films, and lenses would yield the phenomena of the colloidal state, and especially of gelation. The horizontal networks which appear, and which are in an unstable state so far as surface energy is concerned, must represent in a crude way the mechanism of a muscle reduced to two dimensions, for there can be little doubt now that the force of muscular contraction is derived from changes in the energy of surfaces in the interior of each muscle fibre.

Curves of the change of tension produced by the spreading of A upon water, obtained by Wilhelmj's method of measuring surface tension, were given in an earlier paper (*loc. cit.*) and it was noticed that, when disturbance due to hysteresis of the surface is avoided, the curve for certain substances consists of a series of straight lines. I add here the curve for pure oleic acid (fig. 1). The vapour pressure is so low as to render the error due to

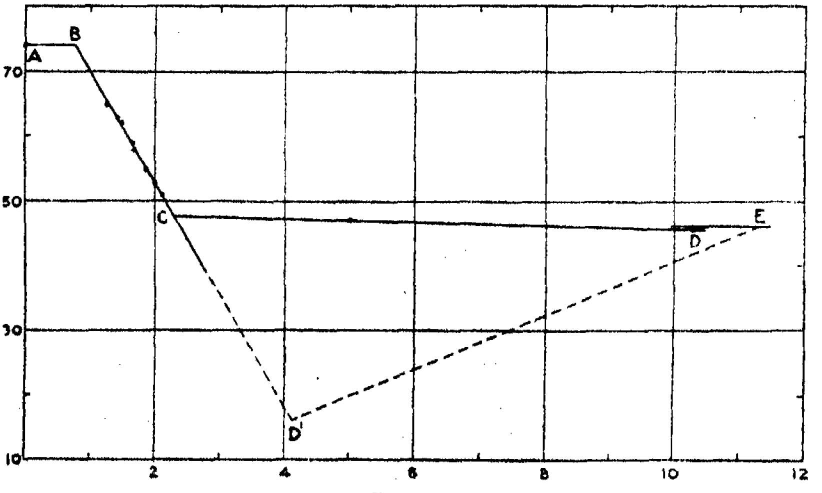


Fig. 1.

vaporisation from the surface negligible, but, unfortunately, the acid leaks past the barriers used to contract the film by diffusion through the body of the water, so that the observed tension tends always to be too high. In time, the oleic acid completely escapes from the control of the barriers, thus a contracted surface of tension 46·2 was left overnight, two barriers close

together confining it. Twenty hours later the tension had risen to 60·9. By again sweeping as much of the acid as possible on to the same restricted area the tension fell to 47·6 at the point marked with a cross in fig. 2. The curve for oleic acid is again the same type of curve—straight lines and sharp inflections. In the previous paper other curves are given in which there is only one sharp inflection and no part beyond this forms a

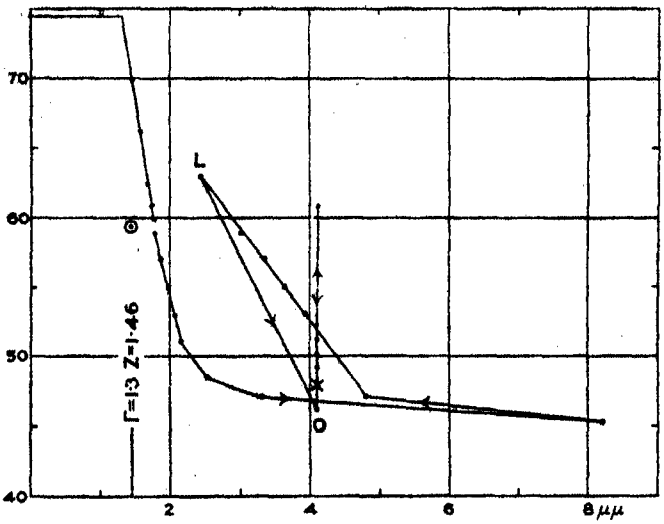


Fig. 2.

straight line. With the fuller knowledge now in my possession I regard such curves as characteristic of films composed of two substances at least, one having an effect on the tension of the surface less than that of the other.*

Measurements of the tension T_{AB} throw some light upon the singular features of these curves. Let it first be supposed possible by avoiding the formation of a lens (as *e.g.* by allowing vapour to condense on to the surface in the absence of nuclei) continuously to increase the mass of A per unit of surface area, a point will be reached when an independent surface of pure A is formed. The curve therefore begins at $T_S = T_B$ and ends at $T_S = T_A + T_{AB}$, both points being determinable by experiment. Of the intervening curve the first portion AB is horizontal or slightly undulating.† Lord Rayleigh interpreted it to be the region in which the quantity of A placed on the surface is insufficient to form a continuous

* The sample of cymene used previously was found to contain a small percentage of an impurity with a high boiling point.

† 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 623.

sheet. The objection to this interpretation is the dimensions of the molecule which follow from experiment. Taking, for instance, pure oleic acid, the depth of the film of acid at the point B is of the order 13×10^{-8} cm. Putting 10^{-8} as the diameter of the hydrogen atom, a molecule of the acid regarded as a sphere would have by the Barlow-Pope theory a diameter of only $4{\cdot}8 \times 10^{-8}$ cm. Perhaps a way out of the difficulty may be found ultimately by treating the point B as a critical point in the electric polarisation of the surface, also the calculated thickness of the film of A may be largely in excess of the real thickness, for complete immiscibility of A and B cannot be postulated, and some loss must occur owing to diffusion into the mass of B.

Lord Rayleigh remarks that "an essentially different result would seem to require a repulsive force between the molecules (of oil), resisting" contraction of the film. There is, as I have already pointed out, evidence to show that the oil spread on the surface is at a different electrical potential to the water. A repulsion due to the charge on each molecule of oil must therefore exist. But this only increases the difficulty, since such a tangential repulsion would, if it operated alone, bring about a fall in the tension before a continuous layer of oil was formed on the surface. It is open to us to suppose that one of the first effects of the oil is to undo a state of affairs at the surface of the water, namely, an average orientation of the water molecules themselves under the influence of the inwardly directed force of attraction, and thereby to increase the tension of the water, but a hypothesis which goes so far beyond ascertained fact cannot be so satisfactory as the direct explanation offered by Lord Rayleigh.

The significance of the inflection at C (fig. 1) is, I think, clear. It is the point where the continuous uniform sheet of A spread on B ceases to be stable and any further added quantity gathers into a lens. This occurs when the tension of the composite plane surface is equal to $T_A + T_{AB}$. The following table confirms this conclusion. T_C is the tension at the point C, as measured by Wilhelmj's method.

Castor oil	$T_C = 58{\cdot}0$	$T_A + T_{AB} = 58{\cdot}27$
Oleic acid	$= 47{\cdot}5$	$= 46{\cdot}30$
Ricinolic acid	$= 48{\cdot}8$	$= 48{\cdot}34$
" "	$= 45{\cdot}0$	
Ethyl hydrocinnamate	(between $55{\cdot}64$ and $58{\cdot}16$*)	$= 57{\cdot}73$
Benzene	$= +64{\cdot}0$†	$= 65{\cdot}4$

* Camphor is still active on a surface on which a lens of this ester is standing, the space above being saturated with the vapour. Rayleigh fixes the camphor point at 57·7.

† In order to maintain the surface against loss by evaporation it is necessary to have a flat lens of benzene, therefore K_g has a sensible value, and the tension observed is slightly lower than T_C.

The slope of the line CD is determined partly by the form of the lens or lenses on the surface, that is to say, by the quantities T_A, T_{AB}, and the density

of the fluid A or D_A; and partly by the circumstance that the abscissæ are calculated from the total mass of A placed on the surface divided by the area. They do not, therefore, any longer represent the true mass of A per unit area of the composite surface, but an average of that quantity and the mass absorbed into the lens. Since this is always greater than the true value, the line CD should slope more steeply than it does in the figure. The point C, therefore, is not the lowest point of the curve. This conclusion follows from other considerations. In the case of chemically saturated substances C ($= T_A + T_{AB}$) lies on or above the level of T_B. In spite of this, vapour of any of these substances condenses on to a surface of pure water and in so doing lowers the tension. Also, as we have already seen, the relation $T_B < T_A + T_{AB}$ holds for all surfaces in which excess of A forms a convex lens on a composite surface of A and B, and such lenses are formed by the condensation of the vapour of carbon tetrachloride, benzene, etc., on to the surface of water. Lastly, the mechanical stability of a film formed from the composite surface is not minimal at C but at a point of lower tension produced by still further concentration of A on to the surface.* The true curve of the variation of tension of the composite surface of A and B, therefore, must fall below the point C to a minimum at D′ and from C to D′ the surface when realised is unstable with respect to lens formation. This explains an otherwise anomalous result which I have thrice obtained with exceedingly pure oleic acid spread on to a very clean surface of tap water (temperatures 14·5° and 11·5°), namely that at a certain point further thickening of the film of acid by contraction of the surface caused a sharp rise of tension which thenceforward remained constant at the higher level even when the film of acid was thickened as much as possible by extreme contraction of the surface. Each step in the contraction now gave rise to a sharp rise of tension, which at once gave way, the tension falling to the constant figure. Inspection of the surface with a hand lens left no room for doubt as to the explanation of the phenomenon, for it was seen to be covered by a dew of very tiny lenses. On extending the surface the dew disappeared just as though the acid had evaporated and the tension now rose and fell normally with movement of the barrier. On again contracting the surface the dew reappeared and the tension at once became practically independent of the area. It is probably not owing merely to accident that this striking phenomenon of supersaturation has been observed only when a substance of high chemical purity was used.

At D′ some new physical factor must come into operation. One supposition open to us is that at D′ the attraction of B for A is fully

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 630.

satisfied. This would make $\Gamma_{D'}/D_A$ equal to the range of the attractive force between the fluids B and A if the density of A on the composite surface be put equal to that of A in mass. Γ is the mass of A per unit area of surface.

The part of the curve D′E, of unknown slope, would then relate entirely to the work expended in forming a layer of a new phase, namely pure A, and the process is complete at E when the tension of the upper face becomes T_A, and that of both faces $T_A + T_{AB}$. The two tensions are now equal to the tension at C, which, however, is that of a single true composite surface.

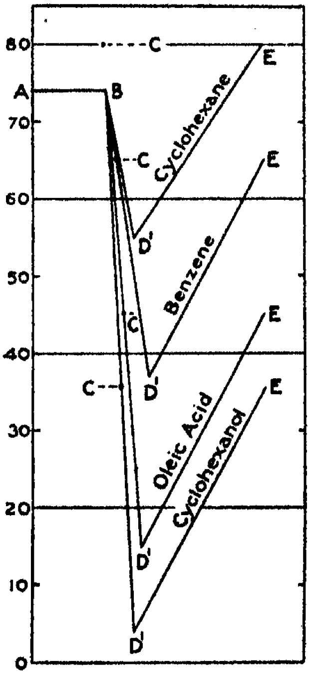


FIG. 3.

The diagram (fig. 3) may serve to make the explanation clearer. On it are shown curves for four substances, the point D′ being in each case put equal to T_{AB}. The scale of the abscissæ and the slope of the lines is entirely arbitrary. At the point C on each curve the tension of the composite surface has fallen to the equality $T_s = T_A + T_{AB}$, save in the case of the chemically saturated substance, when T_S is always $> T_A + T_{AB}$. From C to D′ the composite surface is stable with respect to infinitesimal variations of the mass of A per unit area, but unstable with respect to finite variations. That is to say, a lens cannot form spontaneously, because any tendency to a local accumulation of the fluid A will be resisted by the tension of the surface. But if suitable nuclei are present, or if a lens of A be placed on the surface, condensation must occur. If the curve from B to D′ be a straight line we have, as the equations of this part,

$$\frac{dT_S}{d\Gamma} = -c \quad (1) \qquad \text{and} \qquad T_s = C - c\Gamma, \quad (2)$$

Γ being the mass of A per unit area of surface.

The part D′E is a region of complete instability, hence, as has already been pointed out, when a lens of A is extended to form a sheet, the sheet ruptures when its depth is diminished below a certain minimum. The form and slope of this part are entirely unknown.

The changes of the vapour pressure of A in equilibrium with the composite surface cannot be followed with any certainty, though something may be said about them. At A on the curve the vapour pressure of the fluid A

in a closed space above the surface would of course be zero, and at E it is that of the vapour saturated in contact with pure A in mass. Between these points we have the relation established by Gibbs,* namely

$$dT_s = -\frac{\Gamma}{\gamma}\,dp, \tag{3}$$

in which Γ is the excess of A concentrated on unit area of the surface over what would be there if no concentration occurred. Γ therefore has sensibly the same significance as that given to it in this paper; γ is the density of the vapour. As an approximation we may put $\gamma = p/R\theta$, in which R is the gas constant, and θ the absolute temperature on the thermodynamic scale. Equation (3) now becomes

$$dT_s = -\Gamma R\theta\frac{dp}{p},$$

which for limits Γ_0 and Γ_1, when the vapour is compressed isothermally on to the surface, becomes

$$(T_1 - T_0) = -R\theta\int_{\Gamma_0}^{\Gamma_1}\frac{\Gamma}{p}\frac{dp}{d\Gamma}\,d\Gamma,$$

an equation which can be integrated only if we know the form of the function $dp/d\Gamma$.

Equations connecting the vapour pressure with the tension of the composite surface are given by Warburg† and Cantor,‡ but they cannot be trusted owing to faulty reasoning. In both cases they are derived by equating the balance of work gained to the change in the potential of the surface when fluid is evaporated from A and condensed on to the surface of B, the series of operations performed upon A being essentially those used by Helmholtz§ in his calculation of the change of free energy when a quantity *dm* of water is evaporated from the plane surface of a mass of pure water, and condensed into a solution of salt in water. In the final process, when the water vapour is condensed into the salt solution, Helmholtz puts the pressure constant, and the work therefore simply equal to *pv*. This is correct only if the mass of the salt solution be infinite. Warburg and Cantor follow the procedure of Helmholtz in that they put the pressure of the vapour of A constant while it is being condensed on to the surface of B. This is equivalent to putting T_s constant throughout the operation, and is obviously wrong.

Something may be said in answer to two questions, namely, (1) at what

* 'Trans. Conn. Acad.,' 1878, vol. 3, p. 398.
† 'Ann. Physik u. Chem.,' 1886, vol. 28, p. 394.
‡ *Ibid.*, 1896, vol. 56, p. 492.
§ 'Mem. Phys. Soc.,' vol. 1, Part II.

point on the curve is the vapour pressure of A maximal? and (2) at what point is it equal to that of the vapour tension of pure A?

Equation (3) may be written

$$\frac{dT_S}{d\Gamma} = -\frac{\Gamma}{\gamma}\frac{dp}{d\Gamma}.$$

Since Γ/γ is necessarily positive the curve would begin to ascend when $dp/d\Gamma$ becomes negative—that is, when for any further addition of A to the surface its vapour pressure falls. This would happen along D′E; and the fall in vapour pressure would be strictly analogous to that which occurs when spheres of fluid in equilibrium with vapour about them fuse to form a larger sphere or a plane sheet. At D′, therefore, the vapour pressure of A would be maximal. It would also be supersaturated with reference to a plane surface of A, since along D′E it is falling to the pressure of saturated vapour at E.

Passing backwards from D′ towards C the vapour tension of A at the composite surface is at first greater than the vapour pressure of pure A, and the surface would be in both tensile and vapour equilibrium with a convex lens of A. At some point the tension of the vapour at the composite surface falls to an equality with that of a plane surface of pure A. The point at which this happens will depend upon the pressure of the saturated vapour and, since T_{AB} changes only slowly with temperature, the point would fall lower and lower on the line CE′ as the temperature rises. That this is so appears from measurements made by Clark* of the tension at the interface of ethyl ether and glycerine, and of a surface of glycerine in contact with a vapour space in which the vapour was maintained in equilibrium with the pure ether. The quantity T_S is always $> T_{AB}$ except near the critical point of ether, when it is $< T_{AB}$. It is interesting that in both cases the curves which connect temperature and T_S and T_{AB} respectively are sensibly straight lines. The curve for T_S is at ordinary temperature high above that of T_{AB} but, falling more rapidly, it cuts the latter at about 170°—the critical temperature of ethyl ether being 194°.

The way in which vapour is as it were flung off a surface during spreading points very decisively to a large rise in the tension of the vapour of A at some stage in the process. Ethyl hydrocinnamate boils at 247—249° according to Beilstein, and as it is immiscible with water I hoped this ester would serve for measurements of the change of tension produced by thin films spread on water. It proved, however, to be quite impossible to obtain any measurements owing to the fact that quite large quantities of the ester

* 'Proc. Amer. Acad. of Arts and Sciences,' 1906, vol. 41, p. 361.

evaporate practically completely from the clean surface of water in less than a minute. The evaporation is accompanied by violent currents and eddies on the surface. Measurements of the tension prove that evaporation is not from the fully extended sheet of ester, for, though the excess of each drop placed on to the surface evaporates, a residue remains as a film which causes a permanent fall of tension. Also, when the sheet of ester has been sufficiently thickened by a succession of drops (the larger part of each being lost by violent evaporation) and in that way the tension lowered permanently to $\pm$ 56 dynes, the rapid loss of vapour ceases and a thin extended sheet of ester will lie quietly upon the surface. It would occupy too much space to describe the complicated changes which occur when a lens of this ester is trying to spread over a surface of high tension, but, taken together, they show that the expulsion of vapour occurs only near the edge of an extended lens. Consider what happens when a lens is extended by a higher tension. In the processes of expansion and thinning of the sheet it must be dragged through the whole region of instability and high vapour pressure from E through D′ to C. The only way of escape is for the unstable sheet to gather into small lenses, and this is what continually happens, very small lenses being formed by and cast off from the edge of the main sheet. The result in the main is that the potential energy of a lens of ester standing on a surface of high tension is partly expended in boiling the ester off the surface.

Any explanation of the variation of tension with the varying depth of the film of A to be adequate must include an explanation of the remarkable movements of *e.g.* a pair of lenses of carbon bisulphide on a clean water surface. To exhibit the movements to perfection the lenses must be small and highly convex. If they come within about 1 or 2 cm. of each other they are violently attracted and move directly towards each other until the edges are nearly in contact, when equally violent repulsion occurs. In this way rapid alternate attraction and repulsion occurs, always, if undisturbed, accurately along a line joining the centres.

The explanation is I think as follows:—Consider each lens when out of the sphere of influence of the other. Vapour is being condensed on to the water face to form a film which spreads as a film centrifugally until it is destroyed by evaporation. The lens is thus the centre of an area of lowered tension, which therefore forms a depression. When two lenses come sufficiently close together these depressed areas fuse and a trough is formed between the centres along which they move—the trough deepening as they approach.

With the near approach of the lenses the vapour sheet is thickened until

the tension falls to D′, beyond this there would be an abrupt rise of tension and a repulsion. The obstacle to the fusion of the lenses which is so obvious is the portion D′E of the curve and a pair of lenses must acquire a critical quantity of kinetic energy before they can break through it.

A relation found by Antonoff from measurements of interfacial tensions would, when it holds, fix the vapour pressure of the fluid A at the point C on the curve as very near to that of a saturated solution of A in B. Using partially miscible substances, Antonoff* finds that the interfacial tension is equal to the difference between the tensions of the two phases. That is, in our notation,

$$T_{ab} = T_b - T_a, \tag{4}$$

and at the limit when the fluids are immiscible

$$T_{AB} = T_B - T_A.$$

Clearly the relation is not universal, nor even a very common one, for, taking fluids sensibly immiscible with water, we have

Table II.

	T_B-T_A.	T_{AB}.		T_B-T_A.	T_{AB}.
Cyclohexane	50·0	55	Carbon tetrachloride	50·0	50
Octane	53·4	53	Castor oil	38·7	23
Oil "C"	44·0	61	Ethyl cinnamate	37·0	24
Carbon bisulphide	43·0	56	Ethyl hydrocinnamate	40·5	24

It will be noted that cyclohexane, oil "C," and carbon bisulphide are exceptions to Quincke's rule that T_{AB} is always less than $T_B - T_A$.

I am at a loss how to criticise Antonoff's values, since they purport to be calculated by the erroneous equation $T_S = m/2\pi r$. This would give results 40 to 50 per cent. wrong, but his figures agree with mine in the very low value for the quantity T_{AB} for alcohols, and in the value found for benzene. The values for T'_{AB} calculated from his figures also agree with those found by me for alcohols.

	T_{AB}.	T'_{AB}.
Isoamylic alcohol	4·43	44·59
Isobutyric alcohol	1·76	46·75
Benzene	32·6	34·2

It is possible that though the faulty equation is quoted with approval, the experimental results were obtained with tubes standardised by measuring the tension of some pure fluid whose tension is known.

The explanation of Antonoff's relation is simple, and its theoretical significance not great. If water is saturated with a fluid which causes the tension of water (T_B) to fall, the surface will also become saturated with this fluid. When this happens T_B is reduced to the tension at C on the curve,

* 'Journ. de Chim. Physique,' 1907, vol. 5, p. 372.

which, as we have already seen, is that of a surface saturated with A and is equal to $T_A + T_{AB}$. We therefore have $T_b = T_A + T_{AB}$, and equation (4) now becomes

$$T_{ab} = T_A + T_{AB} - T_a,$$

which, since T_a is always sensibly equal to T_A, means that T_{ab} is sensibly equal to T_{AB}, and this has already been found to be the case.

The portion of the curve BD in the diagrams is drawn as a straight line for reasons which are given in an earlier paper. The curves which Lord Rayleigh gives of the changes of tension with variation in the thickness of a film are gradually bending lines,* and from theoretical considerations he concludes that the tension of a composite surface of A spread on B should vary as the square of the thickness of the film of A.† The question, in the long run, must be decided by experiment, and I therefore add a table of constants (Table III) calculated from measurements of tension by Wilhelmj's method, the thickness of the film of A being varied by contracting the surface with movable barriers.

The method of thickening a film by sweeping it up on to a contracted area by blades is open to many objections. Though leakage of the surface past the barriers may be avoided, loss by diffusion must occur to some extent, since perfect immiscibility cannot be postulated. A contracted film of pure oleic acid in 20 hours had again distributed itself evenly over the entire surface, largely, so far as I could determine, by diffusion through the body of the water. There is thus always a decrement which tends to make the curve bend away from the axis of tension. The result of many measurements is to show that the more accurately and rapidly the series of measurements are made the more closely does the curve approximate to a straight line.

The most successful series I was able to obtain with oleic acid is plotted in fig. 4, and the constants are given in the third column of Table III. Three barriers were used to contain the film and, as far as possible, kept touching each other throughout. The water used was carefully cleaned tap water. The readings were taken rapidly and were very steady until the first inflection of the curve at M; here, owing to some unknown cause, leakage occurred, the tension rising while the weight was being recorded. At N the tension rose abruptly to O owing to the formation of exceedingly fine lenses, each of which appeared under a hand lens as little more than a point. A further slow rise from O to P occurred in nine minutes, and during this nine minutes some lycopodium dust drifted 2·5 cm. away from the barriers on the side

* 'Phil. Mag.,' 1899, [5], vol. 48, p. 331.
† *Ibid.*, 1892, vol. 33, p. 468.

remote from the contracted film of oleic acid. The rise OP therefore was due to a very slow leakage past the barriers.

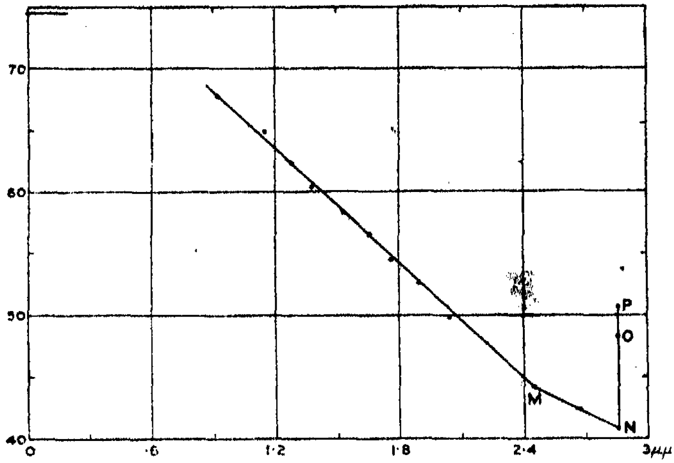


Fig. 4.

Table III.

Ts.	C_i.	C_{ii}.	C_{iii}.	C_{iv}.
72 ·4	28528			
71 ·8	26188			
70 ·85	25612			
69 ·9	27892			
68 ·9	28652			
67 ·8	—	—	15 ·658	
67 ·0	27450			
66 ·0	—	—	—	15238
65 ·4	—	—	—	15086
64 ·9	—	—	15 ·127	
63 ·9	—	—	—	15070
63 ·5	—	—	—	15316
63 ·0	26503			
62 ·5	—	—	15 ·562	
62 ·0	—	17890	—	15180
60 ·4	—	—	15 ·880	15198
59 ·0	26831	18067	—	15252
58 ·5	—	—	15 ·528	
58 ·0				
57 ·0	20045			
56 ·5	—	18000	15 ·443	14960
55 ·0				
54 ·6	—	—	15 ·694	
53 ·0	—	17415		
52 ·6	—	—	15 ·567	
51 ·0	—	17403		
49 ·9	—	—	15 ·796	
44 ·25	—	—	15 ·486	
42 ·5	—	—	14 ·831	
40 ·9	—	—	14 ·457	

C_i, C_{ii}, C_{iii} refer to three separate measurements made with pure oleic acid. C_{iv} to castor oil. C_i, C_{ii}, C_{iv}, the constants are in arbitrary units. C_{iii}, the units are dynes per linear centimetre and 10^{-7} cm.

The particular form of the curve near the second inflection (at point C) depends upon the conditions which favour or hinder lens formation such as the number and nature of solid particles or other nuclei in the surface film, and is not of very great theoretical interest. Sometimes the inflection is remarkably sharp, at others it is gradual.

If the curve be a straight line, then we have

$$\frac{dT_S}{d\Gamma} = -c \quad \text{and} \quad T_S = C - c\Gamma,$$

C being the integration constant. This last equation may be written

$$T_S = T_B - c(\Gamma_S - \Gamma_0), \tag{5}$$

Γ_0 being the mass of A per unit area of surface at the point C in the curve.

The relation $dT_S/d\Gamma =$ constant is of considerable theoretical interest if it can be established, for let us consider a composite surface formed by removing a layer of depth Δ from A and applying it to B. Then if ΔT_A is the work expended per unit area in removing the layer from A to ∞ and $2\Delta T'_{AB}$ the work gained from the attraction of B for A in bringing it to rest on B we have

$$T_S = \Delta T_A + T_B - 2\Delta T'_{AB}.$$

Let ρ_A, ρ_B be respectively the density of the fluids A and B, then if $m\rho_A\psi_A(z)$ is the attraction between a mass m of A distant z from an infinite mass of A and the latter, the work needed to remove to infinity a sheet of thickness dz is, per unit area, $\rho_A^2\int_z^\infty \psi_A(z)\,dz$.

Call this integral $\theta_A(z)$, then ΔT_A becomes equal to $\rho_A^2\int_0^\Delta \theta_A(z)\,dz$.

Similarly, $$2\Delta T'_{AB} = \rho_A\rho_B\int_0^\Delta \theta_{AB}(z)\,dz,$$

and we have $$T_S = T_B + \rho_A^2\int_0^\Delta \theta_A(z)\,dz - \rho_A\rho_B\int_0^\Delta \theta_{AB}(z)\,dz$$

and $$\frac{dT_S}{dz} = \rho_A^2\theta_A(z) - \rho_A\rho_B\theta_{AB}(z).$$

But $$\Gamma = \Delta\rho_A \quad \text{and} \quad d\Gamma = dz\rho_A, \tag{6}$$

therefore $$\frac{dT_S}{d\Gamma} = \rho_A\theta_A(z) - \rho_B\theta_{AB}(z); \tag{7}$$

and, since $\frac{dT_S}{d\Gamma}$ is by experiment equal to a constant,

$$\theta_A(z) = \frac{\rho_B}{\rho_A}\theta_{AB}(z) + \beta, \tag{8}$$

where β is another constant.

$\theta_A(z)$ is the function of the potential of A at the surface of A, and $\theta_{AB}(z)$ of A at the surface of B, hence we may conclude that if $dT_B/d\Gamma$ is equal to a constant the form of these functions must be the same.

We may perhaps proceed a stage further. Laplace assumed that the function of the attractive force between matter at minute distances is the same in all cases, "the attraction differing merely by coefficients analogous to densities in the theory of gravitation." On this assumption we may write equation (7)

$$\frac{dT}{d\Gamma} = \alpha\theta_A(z), \tag{9}$$

and $\theta_A(z)$ is then seen to be a constant, a result which is in agreement with the suggestion of Young that molecular attraction is a force which is constant in magnitude over the very minute range through which it acts. But the range in question must be less even than the thickness of the films of oil which when spread upon water reduce the tension, for, if $\theta(z)$ be constant, then since $d\theta(z) = -\psi(z)$ this last function is equal to 0. The physical significance of this last relation would be that each layer of molecules of A spread on the surface is attracted only by the layer of molecules previously there with which it comes into contact, a result not inconsistent with many aspects of this difficult question but altogether inconsistent with the view that the attraction of B for A ceases only at the point D′ in the curve.

Though such conclusions, based as they are upon an assumption of uniform density throughout an interface, cannot have great value, they are interesting as pointing to an unexpected simplicity in molecular forces. The simple spatial relations which are the essence of the Barlow-Pope theory of the molecular structure of close-packed forms of matter also seems to demand some simple law. If there were, for instance, alternating zones of attraction and repulsion about each molecule, more than one arrangement in space would satisfy the condition of minimal potential, and it would be possible by adequate pressure to compress a fluid to a volume which it would continue to occupy when the pressure was lowered.

The unexpectedly simple relation $dT/d\Gamma = -$ a constant would appear to hold for an interface between solid and fluid. A large amount of work has shown that when a solute such as iodine is condensed on to the surface of, for instance, animal charcoal, the equilibrium reached is given by the empirical equation $m = Kc^{1/n}$, where m is the mass of the solute condensed on to the surface, c the final concentration of the solution, and k and n are parameters. Putting the area of the surface of the solid as unity, this may be written

$$\gamma = \alpha\Gamma^n,$$

which on differentiating gives

$$d\gamma/d\Gamma = \alpha n\Gamma^{n-1} = n\Gamma/\gamma.$$

By comparison with Gibbs' equation $\Gamma = -\frac{\gamma}{R\theta}\frac{dT}{d\gamma}$, we get

$$\frac{dT}{d\Gamma} = -nR\theta.$$

Hence for an isothermal change $dT/d\Gamma$ is a negative constant.

Another significance of the constant c in (5) must not be lost sight of. Comparing the relation $dT_S = -c\,d\Gamma$, with the similar equation for volume energy $(dP) = K d\gamma$, in which γ is the mass in unit volume, we see that C corresponds to K which in the gas equation is the gas constant R. But, whereas R implicitly refers to a zero of temperature, namely, the absolute zero, the constant c is related to the temperature of complete miscibility of A and B when T_S is zero.

If the fields of force about a molecule are not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the centre of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random disposition which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must therefore have a characteristic molecular architecture, and the condition of minimal potential involves two terms, one relating to the variation in density, the other to the orientation of the fields of force.* When the composite surface is formed its architecture is determined by the interaction of the fields of force of molecules of A and B under the influence of the attraction of B for A. When the structure is complete the tension T_{AB} is reached and any further addition of molecules of A to the surface does not disturb the architecture. But, just as there are in many cases two arrangements of the same molecules in the solid state, that of the glass, and that of the crystal, the former containing the greater quantity of energy per unit of mass, so in the formation of these films of matter the architecture actually reached may not always be that of least potential.

Description of Figures.—Save for the diagram fig. 3 the scale of the ordinates is dynes per linear centimetre, that of the abscissæ 1×10^{-7} cm.

* Lord Rayleigh ('Phil. Mag.,' 1892, vol. 33, p. 209) has shown that the deviations from Fresnel's formula for the reflection of light at a liquid surface may be traced to the presence of a film of impurity on the surface. The residual deviation which persists when all such films are swept away may, perhaps, be attributed to the real surface film of the pure fluid.

($\mu\mu$), calculated from the weight of acid spread on the surface on the assumption that the density of the film is that of oleic acid in mass. Fig. 1 is plotted from a particular experiment with pure oleic acid—that is to say with the purest acid which Kahlbaum prepares, further purified by fractional crystallisation. The line BC has been followed by Miss Pockell's method into the unstable region CD′, until the end of the continuous line. The horizontal line through E marks the tension which is equal to the sum of the tension of the pure acid and that of the interface between acid and water or $T_A + T_{AB}$. Fig. 2 illustrates a prolonged experiment with oleic acid. The curve is interrupted at one point where there was an accident to the balance, the result being to alter the slope of the curve. The curve was followed without pause, save for the accident just alluded to, to the point O, when the barriers were left in position. The tension rose in 10 minutes to the first dot, and 20 hours later it was found to be at the top of the vertical line. By again concentrating as much as possible of the oleic acid on to the same area the tension fell to the point marked with a thick cross. The contraction of the surface from L to O was made very rapidly. The ringed dot marks the tension when 0·1 mgrm. of oleic acid was spread on to a surface of clean distilled water 685·7 cm.^{2} in extent. For this tension therefore $\Gamma = 1{\cdot}3 \times 10^{-7}$ grm. and $z = 1{\cdot}46\ \mu\mu$. The scale of the abscissæ is based upon this measurement. The remaining figures are adequately explained in the text.

Appendix 1.—In a previous paper* I pointed out that the mechanical stability of a composite surface is maximal just beyond the point B in the curve when the tension begins to fall. The measure of mechanical stability was the time which elapsed between the formation and bursting of bubbles of a particular size on the surface. The rise in mechanical stability from zero to a maximum was found to occur at a point some distance lower on the curve than B. The reason for this displacement is simple. When a film is formed at the surface by allowing a bubble of air to ascend from below, the surface is stretched and the quantity Γ, that is the concentration of the fluid A spread upon the water, thereby diminished. The effect is to put the state of the surface backwards along the curve towards the inflection at B. If the film is sufficiently stretched, that is if the bubble is large enough to make $\Gamma < \Gamma_\beta$, the bubble at once bursts. The amount of displacement of the rise of mechanical stability forwards along the curve is thus a function of the radius of the bubble of air. With infinitely small bubbles it would coincide with the inflection at B, where theory would place it.

Appendix 2.—An attempt to measure the tension of a composite surface in

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 627.

equilibrium with the saturated vapour of cyclohexane failed and the failure is instructive. Let a large lens be formed on the surface of water in a closed space. When the vapour pressures are in equilibrium since the lens of cyclohexane is sensibly flat the vapour tension must be that of saturated vapour. In order to calculate the tension of the composite surface of water and condensed vapour of cyclohexane we have the relation

$$T_S = T_A + T_{AB} - \tfrac{1}{2}g(D_A h^2 - D_A h'^2 + D_B h'^2)$$

and the hydrostatic equation

$$D_A h = (D_B - D_A) h'.$$

h and h' refer respectively to the height of the upper surface of the lens above the surface of the water and the depth of the lower surface below it; h and h' very approximately can be got by measuring the area of the lens and its volume, and taking the thickness as uniform.

I found that when placed on tap water of tension 73·6, the vapour space being small, 0·5 c.c. cyclohexane formed a lens 6·4 cm. in horizontal diameter, 2 c.c. a lens 13·5 cm. diameter. The last term is negligible for lenses so thin (0·015 cm. and 0·014 cm. respectively), and T_S calculated is 79·34 and 79·35. Clearly, therefore, T_{AB} must have been reduced by the accumulation at the interface of some trace of impurity. The changes observed agree with this, for the cyclohexane when first put on forms a convex lens which slowly flattens out. The flattening cannot be due to an increase in T_S above T_B since the condensed vapour lowers the tension, as is readily seen by admitting a little air so as to relieve the concentration of the vapour of A, when the flattened lens at once contracts.

Appendix 3.—The arguments employed in this paper throw light upon a suggestion put forward by Laplace, and incidentally on that vexed point the physical significance to be attributed to the term "density" as used by Laplace. By the Young-Laplace theory we have for the intrinsic pressure and the surface tension of a fluid respectively

$$\kappa = 2\pi\rho_2 \int_0^\infty \psi(z)\,dz \quad (10) \qquad \text{and} \qquad T = 2\pi\rho_2 \int_0^\infty z\psi(z)\,dz. \quad (11)$$

Laplace assumes that $\psi(z)$, like gravity, is a function depending only on the density of the substance, and we may therefore write

$$T = \rho^2 T_0 \quad (12) \qquad \text{and} \qquad T'_{AB} = \rho_A \rho_B T_0. \quad (13)$$

From (10) and (12) follows

$$T_{AB} = (\rho_A - \rho_B)^2 T_0.$$

It has been objected that the facts do not accord with this relation. This

is true, but the cause may lie either in the fact that T_0 is constant only for similar fluids—that is for fluids of the same chemical type, or in the difficulty in identifying the density of Laplace's theory with a particular physical property.

Comparing equations (3) of the paper preceding and (12) we get

$$\rho_0^2 T_0 = \frac{(\tau-d)}{v^{2/3}}\kappa.$$

If the density be taken as a molecular quantity then $\rho = 1/v$ and $T_0 = (\tau-d)\,\kappa V^{-\frac{2}{3}}$. From this we can derive equation (4) of the preceding paper as the expression for the interfacial tension.

The expression $T_{AB} = (\rho_A - \rho_B)^2 T_0$ is now seen to be wrongly derived, the false assumptions being the identity of κ_A with κ_B, and of $(\tau_A - d)$ with $(\tau_B - d)$. And for a similar reason the expression $T'_{AB} = \rho_A \rho_B T_0$ is inadmissible.

A Simple Method of Finding the Approximate Period of Stable Systems.

By A. Mallock, F.R.S.

(Received February 21,—Read March 13, 1913.)

In practical engineering work it is often a great convenience to be able to find the period of a structure, the calculation of which, by ordinary mathematical processes, would be difficult or even impossible. To find the period of a structure for any particular mode of vibration involves a knowledge of its stiffness (regarded as a spring) and of the distribution of the mass, but if the latter is known, even approximately, a knowledge of the period gives the stiffness, and the deflections for a given load can be found by simple arithmetic.

In nearly every case likely to occur in practice a stable structure can be represented, as far as its elastic displacements are concerned, by an equivalent pendulum, a pendulum, that is, which has the same period as the particular mode of vibration under consideration, and an effective mass equal to that part of the mass of the structure which is subject to vibration, but concentrated at what, for the present purpose, may be called the centre of oscillation.

The proposition on which the simple determination of period above referred to depends is as follows :—

Let the length of the equivalent pendulum be l, and let σ be the stiffness of the structure, so that the force required to cause a displacement x measured at the centre of oscillation is σx. Now let x_1 be taken so that $\sigma x_1 = W$ where W is the weight of the structure. The period τ is given by either of the equations $\tau = 2\pi\sqrt{(l/g)}$ or $\tau = 2\pi\sqrt{(W/g\sigma)}$,

$$\therefore\ l/g = M/\sigma, \quad \text{and since} \quad \sigma = Mg/x_1, \quad M/\sigma = x_1/g, \quad \therefore\ x_1 = l.$$

That is the deflection x_1 (the deflection, namely, caused by a force equal to the weight of the structure) is equal to the length of the pendulum which has the period of the structure.

This statement applies accurately to all cases where the mass is concentrated at one place, or where the structure moves without deformation or rotation, and in which, consequently, the mass may be supposed to exist only at the centre of inertia. In other cases the application is approximate, but by a judicious choice of position at which the deflection is measured, or of the assumed distribution of the mass, the approximation may be made very close.

A few examples will indicate the uses to which the proposition may be turned—

(1) A rod or pole, ballasted to float upright in a fluid, has the same up and down period as a pendulum whose length is the depth of statical immersion. The only correction to be applied here is that for the inertia of the fluid set in motion; this is known for many forms and tends towards zero when the rod is long and thin.

(2) A spiral spring which is compressed through the unit of length by the action of N units of weight is loaded with a weight W. The compression due to the load is $W/N \times$ unit of length, and the approximate period is $2\pi\sqrt{(W/Ng)}$. The correct period can be found by adding one-third of the weight of the spring to the load.

(3) A girder of known weight is deflected N units of length by a central or terminal load equal to its own weight. The approximate period when unloaded is $2\pi\sqrt{(N/g)}$. If the section of the girder is uniform, a closer approximation may be obtained if the deflection is measured at a quarter of the half length from the centre in the case of a girder supported at both ends, or a quarter of the length from the free end when fixed at one end only.

(4) A ship which has a mean draught N feet of water has pitching period dependent on the draught and on its moment of inertia about the axis of pitching. If the ship had no rigidity and behaved as if made up of a number of detached vertical cross-sections floating at the mean draught, the pitching period would be nearly $2\pi\sqrt{(N/g)}$. A correction is required for rigidity and also for the inertia of the water involved in the motion. The

first of these corrections is small for ships of ordinary proportions, and decreases with the ratio of draught to length. The second increases the period (as calculated from the formula) by something like 10 per cent. The precise amount depends on the ship's "lines."

(5) If a vertical column when struck is found to give a note of a certain pitch, the principle here used allows of the immediate determination of its flexure under any given lateral force, and if the nature and dimensions of the column are known, the pitch under no load can be determined from first principles. As the load on the ends increases, the natural period increases also, becoming infinite when the unstable condition is approached and hence the observation of the actual pitch gives a measure of the load which is borne.

I first noticed the relation here stated in 1878, and since that time have found it of great use in almost countless investigations, but except for one case (involving the same principle) referred to by D. Bernoulli it does not, so far as I am aware, appear to have been stated in any publication.

[*April* 10, 1913.—Dr. Schuster has pointed out to me that there were mistakes in the original text of examples (2), (3), and (4). These have now been corrected.—A. M.]

The Motion of Electrons in Gases.

By Prof. J. S. TOWNSEND, F.R.S., and H. T. TIZARD.

(Received February 25,—Read March 13, 1913.)

1. The methods of investigating the motion of negative ions in gases at low pressure that have been explained in some previous papers may be extended to cases in which larger variations are made in the electric force and pressure. In order to find the kinetic energy of the motion of agitation of the ions, the velocity in the direction of an electric force, and the value of e/m for different forces and pressures, it is necessary to investigate experimentally two properties which are characteristic of the motion of electrons. These are the abnormal lateral diffusion of a stream of ions moving in a uniform electric field, and the deflection of the stream produced by a small transverse magnetic force. In the previous experiments the two phenomena were investigated separately and in each case with apparatus which gave satisfactory results when small electric forces were used and the pressures were limited to a certain range. In order to investigate the motion under larger forces an apparatus of more suitable dimensions was constructed, by means of which both the required sets of experiments may be made.

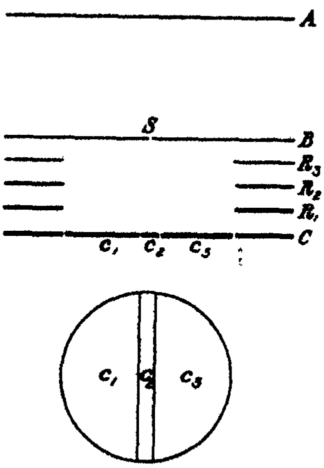


FIG. 1.

2. The negative ions were generated by the action of ultra-violet light on the plate A, fig. 1, and after traversing the distance from A to B some of the ions passed through a narrow slit S, 2 mm. wide and 15 mm. long, in the centre of the metal sheet B. The electric force was in the same direction on the two sides of B, so that the ions, after passing through the slit, continue their motion towards the plane electrodes C, which were parallel to the plane of B. The electrodes C were 4 cm. from B, and three flat rings, R_1, R_2, R_3, 7 cm. internal diameter, were fixed at distances of 1, 2, and 3 cm. respectively from the plane of the electrode C. A separate connection for each ring and for the plates A and B was brought out through a large ebonite plug fitted in the brass cover of the apparatus, and was maintained at a potential proportional to the distance of the corresponding ring, or plate, from the electrodes C. The stream of ions

that came through the slit moved in a uniform electric field and was received by the three insulated electrodes c_1, c_2, and c_3. These were portions of a disc 7 cm. in diameter, the central section c_2 being 4·5 mm. wide and separated from the two equal side plates c_1 and c_3 by air gaps 0·5 mm. wide. The narrow gaps between the electrodes were parallel to the direction of the slit in B. In the calculations it will be supposed that the electrode c_2 is 5 mm. wide, and that the side plates c_1 and c_3 come within 2·5 mm. of the central line.

When no magnetic force is acting the charges n_1 and n_3 received by the electrodes c_1 and c_3 were equal and the centre of the stream fell on the centre of c_2. If n_2 be the charge received by c_2 the ratio $n_2/(n_1+n_2+n_3)$ depends on the electric force Z and the velocity of agitation of the ions.

In the previous experiments the factor k by which the energy of agitation of the ions exceeded that of the surrounding molecules was deduced from observations of the lateral diffusion of a stream of circular section after traversing a distance of 7 cm. under the action of the electric force. The stream was received on a small circular electrode in the centre of a large metal ring, so that the proportion of the charge received by the small disc diminishes rapidly as the motion of agitation increases. The apparatus was therefore suitable for determining the smaller values of the quantity k.

The apparatus described above was better suited for the determination of large increases in the velocity of agitation and the values of k may easily be found from the ratio $n_2/(n_1+n_2+n_3)$, as is seen from the following investigation.

3. Let the origin of co-ordinates be taken in the centre of the slit, the axis of z being normal to the plate B and the axis of y parallel to the length of the slit. Since the central electrode c_2 is much longer than the slit the diffusion in the direction y does not affect the number of ions that are received on the electrode c_2, and it will only be necessary to find the motion in the directions x and z.

Considering the ions that pass at a uniform rate through a narrow section in the centre of the slit parallel to the axis of y, the distribution in the electric field when the motion becomes steady is given by the equation*

$$\nabla^2 n = \frac{Ne}{\Pi} \cdot \frac{Z}{k} \cdot \frac{dn}{dz}.$$

When the electric force Z is measured in volts per centimetre, and the values of the constants Ne and Π are substituted, the equation becomes

$$\nabla^2 n = 41 \frac{Z}{k} \cdot \frac{dn}{dz}.$$

* J. S. Townsend, 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 469.

At the electrodes C ($z = 4$) the number of ions received on an area between the parallel lines $x = 0$ and $x = a$ is proportional to $\int_0^a \int n \, dy \, dx$.

As the ions move in a very wide space they do not extend to the rings R forming the boundary, so that when integrating along the axis of y from one end of the field to the other, the values of n and dn/dy are zero at the boundary. The above equation on integration with respect to y becomes

$$\frac{d^2q}{dx^2}+\frac{d^2q}{dz^2}-\frac{41\,Z}{k}\cdot\frac{dq}{dz} = -\left[\frac{dn}{dy}\right] = 0,$$

where $q = \int n \, dy$, the integration being taken between two points on the boundary.

The series of sines that represents the solution of the equation converges very slowly owing to the nature of boundary conditions, so that it is necessary to express the solution in a more practical form.

Since the principal motion is in the direction of the electric force Z, the ions move in a narrow stream when Z/k is sufficiently large, and the quantities dq/dz and d^2q/dz^2 are small compared with d^2q/dx^2. For a first approximation the value of q may therefore be obtained from the equation

$$\frac{d^2q}{dx^2}-\frac{41\,Z}{k}\cdot\frac{dq}{dz} = 0.$$

With the values of Z/k that occur in the experiments the error introduced by neglecting the term d^2q/dz^2 is probably smaller than the experimental error. It thus appears that the distribution of the quantity q as expressed in terms of x and z is the same as the distribution of temperature ϕ, in terms of x and t, in an infinite solid initially at zero temperature throughout, except at the plane $x = 0$ where the temperature has a constant value ϕ_0 when $t = 0$. The temperature is obtained from the equation

$$\frac{d^2\phi}{dx^2} = \frac{1}{K}\cdot\frac{d\phi}{dt},$$

and the solution given by Fourier is $\phi = At^{-\frac{1}{2}}\epsilon^{-x^2/4Kt}$.

In the problem of the distribution of ions in the space between the plates B and C the surface conditions are $q = 0$ when $z = 0$ for all values of x except $x = 0$, so that q in terms of x and z is given by the equation

$$q = Az^{-\frac{1}{2}}\epsilon^{-\frac{41Z}{4kz}x^2}.$$

The distance z of the electrodes c from the origin was 4 cm. and the central electrode was 5 mm. wide, so that the ratio R, of the charge n_2 received by the central electrode to the total charge $n_1+n_2+n_3$, is

$$\mathrm{R} = \frac{n_2}{n_1+n_2+n_3} = \frac{\int_0^{0\cdot 25} \epsilon^{-2\cdot 56\, \mathrm{Z}_1 x^2} dx}{\int_0^{\infty} \epsilon^{-2\cdot 56\, \mathrm{Z}_1 x^2} dx} = \frac{\int_0^{0\cdot 4\sqrt{\mathrm{Z}_1}} \epsilon^{-y^2} dy}{\int_0^{\infty} \epsilon^{-y^2} dy},$$

where $\mathrm{Z}_1 = \mathrm{Z}/k$.

When various values are given to the quantity Z_1 the corresponding ratios R may be obtained from the tables of the values of the integrals.

It is necessary to take into consideration the width of the slit, since with the larger values of Z/k the proportion of the ions coming through a section of the slit near the edge that arrive on the central electrode is somewhat less than the proportion of those that come through at the centre. The exact proportion for any section of the slit is easily calculated and the ratio $\mathrm{R} = n_2/(n_1+n_2+n_3)$ when the ions come through all sections of the slit equally may be found in terms of Z.

The curve, fig. 2, gives the values of R in terms of $\mathrm{Z}_1 = \mathrm{Z}/k$.

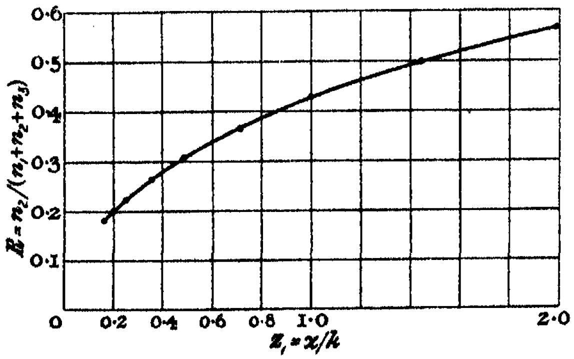


Fig. 2.

4. When the ratio R is determined experimentally with an electric force Z acting between B and C, Z_1 may be found from the curve, fig. 2, and the corresponding value of $k = \mathrm{Z}/\mathrm{Z}_1$ may be determined.

The curves, fig. 3, give the values of $\mathrm{R} = n_2/(n_1+n_2+n_3)$ found for air at various pressures. The ratio R corresponding to a given force and pressure depends on the dryness of the gas. When the pressure is reduced to the required value, R may be observed at intervals while the small quantity of moisture in the apparatus is removed slowly by the phosphorus pentoxide. As the air dries the value of R diminishes and after some weeks a constant minimum value is attained. The continuous curves, fig. 3, represent the minimum values obtained for dry air with different forces and pressures.

Several experiments were made with air which had not been dried very completely. The values of R are then practically the same as those obtained

with dry air when the larger forces are acting. With the smaller forces the moisture reduces the divergence of the stream and comparatively large values of R are obtained. For a certain range of small forces the quantity $k-1$

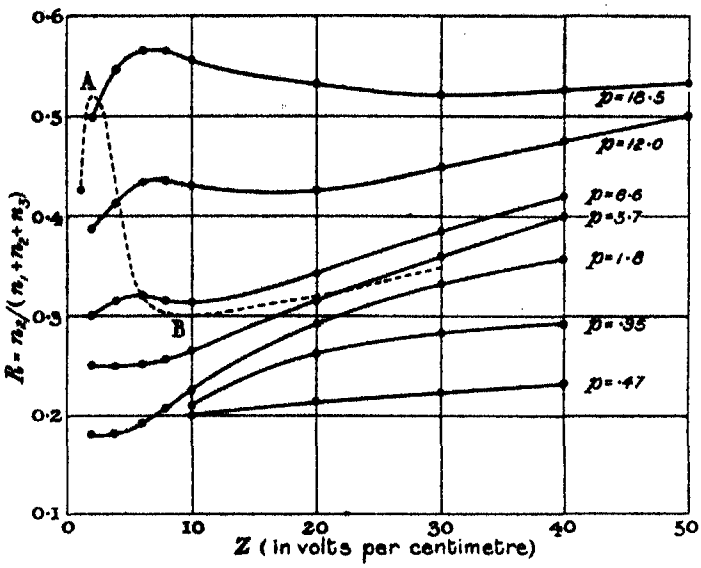


FIG. 3.

becomes very small, and the curve giving R in terms of Z coincides with the theoretical curve, fig. 2. In these cases R is independent of the pressure and the amount of water vapour present, provided the amount exceeds a certain small value.

The dotted curve, fig. 3, illustrates the behaviour of air containing a small quantity of moisture, the pressure being 2·7 mm. With a force of 1 volt per centimetre ($Z = 1$), $R = 0{\cdot}425$, which is the value of R in the theoretical curve at the point $Z/k = 1$. The two curves continue to coincide for some distance as Z increases, but when Z becomes 2 volts per centimetre, R, as determined experimentally, is 0·52, the theoretical curve giving 0·565 when $Z/k = 2$. The value of Z/k corresponding to the ratio 0·52 is 1·6, so that $k = 1{\cdot}25$ when $Z = 2$. The value of R reaches a maximum at A ($Z = 2$), and an increase in the force is accompanied by a remarkable increase in the divergence of the stream. The ratio R attains a minimum value 0·3 at the point B where $Z = 8$, the value of k being $8/0{\cdot}46 = 17{\cdot}4$. Further increases in the force cause the divergence to diminish, and gradually the dotted curve takes a place between the two curves for dry air at 3·7 and 1·8 mm. pressure. For values of Z exceeding 30 the values of R are practically the same as for dry air at 2·7 mm. pressure.

This shows that the electrons adhere to the water molecules and the velocity of agitation of the charged particles is normal, when the force is small. For large forces the effect of the water vapour disappears, and the electrons move freely with a kinetic energy of agitation exceeding that of the surrounding molecules by the factor k. In the particular example illustrated by the dotted curve the effect of the water vapour disappears rapidly between the points A and B and when the force exceeds 30 volts per centimetre the electrons move as in dry air.

When the amount of water vapour increases, the ratios R and the forces Z, corresponding to the maximum and minimum points A and B, increase.

For different pressures p, when the amount of moisture is approximately proportional to the total pressure, the forces corresponding to the points A and B are also approximately proportional to the pressure. This is interesting, from a theoretical point of view, since these properties of the electrons depend on the velocity acquired between collisions with molecules, so that any particular effect should be obtained with the same value of Z/p if the proportion of the different gases that are present is not altered when the total pressure is altered.

5. The values of k for dry air were obtained from the curves, fig. 3, and it was found that k depends on the ratio Z/p. This is shown by the following examples of the numbers obtained from experiments at different pressures when Z/p is approximately constant:—

p.	Z.	Z/p.	k.	W.
18·5	40	2·16	24·0	$1·75 \times 10^6$
12·0	30	2·5	26·0	$1·97 \times 10^6$
1·8	4	2·2	24·0	$1·9 \times 10^6$
3·7	40	10·8	46·0	$5·5 \times 10^6$
1·8	20	11·1	46·5	$5·6 \times 10^6$
0·95	10	10·5	45·5	$5·4 \times 10^6$

The agreement between the different determinations for values of Z/p between 0·2 and 0·5 was not as accurate as with the higher values. This is probably due to the fact that small quantities of impurities have more effect when the lower forces are acting.

The results of the experiments on the lateral diffusion may be represented by a single curve giving k as a function of Z/p. The smaller values of k from $Z/p = 0·2$ to $Z/p = 20$ are given in the curve, fig. 4, and the larger values from $Z/p = 20$ to $Z/p = 200$ are given in the curve, fig. 5.

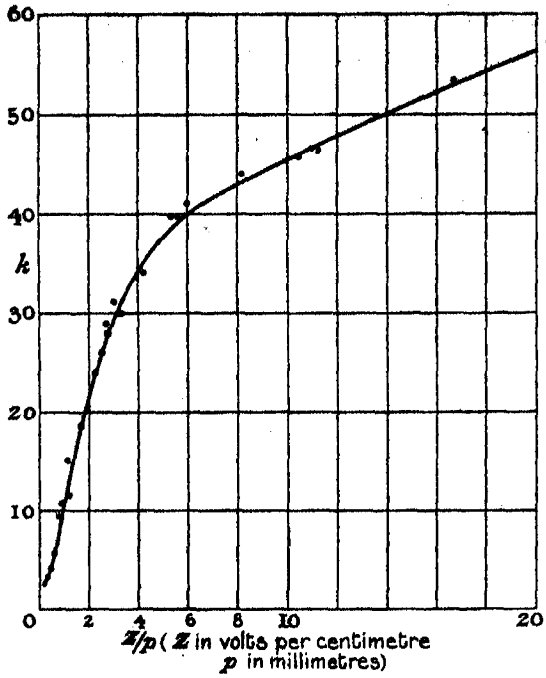

60
50
40
k
30
20
10
0
2
4
6
8
10
20
Z/p (Z in volts per centimetre
p in millimetres)

FIG. 4.

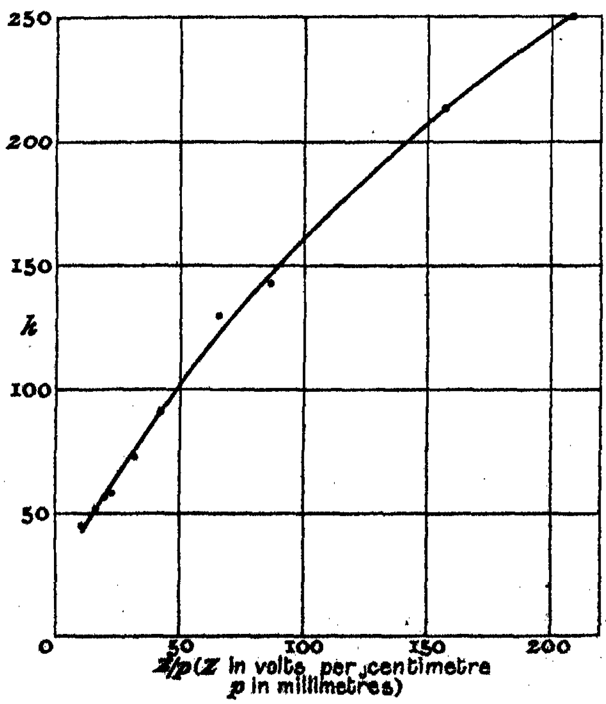

250
200
150
k
100
50
0
50
100
150
200
Z/p (Z in volts per centimetre
p in millimetres)

FIG. 5.

The results thus obtained are in good agreement with previous determinations obtained with negative ions generated by Röntgen rays, and the values obtained by Haselfoot for ions generated by ultra-violet light.

The conclusions to be drawn from these experiments depend on certain formulæ that have been obtained for cases in which the velocity of agitation of the ions is large compared with the velocity under an electric force. It will be seen from these investigations that when Z/p exceeds 0·2 the ions in dry air are in the electronic state, so that the value of e/m may be taken as $5{\cdot}3 \times 10^{17}$. The value of e/m for a molecule of air being 10^{13}, the masses are in the proportion $5{\cdot}3 \times 10^{4} : 1$, so that the velocity of agitation of an electron in thermal equilibrium with air is 230 times the velocity of agitation of a molecule of air, or 10^7 cm. per second. The actual velocities of agitation when electric forces are acting exceed this value by the factor $\sqrt{k}$. In order that the ordinary formulæ derived from the kinetic theory of gases should apply to the motion of the electrons it is necessary that the velocity W in the direction of the electric force Z should be considerably less than the quantity $\sqrt{k} \times 10^7$.

6. The velocities W were determined with the same apparatus for the same forces Z and pressures p.

A transverse magnetic force G was produced by a current in a pair of large circular coils outside the apparatus, the direction of the force being parallel to the slits. The stream was then deflected so that the centre no longer fell on the centre of the electrode c_2 and the charge acquired by the electrode c_1 increased with the force G. In these experiments the electrodes c_2 and c_3 were joined and the current in the coils was adjusted until the charge n_2+n_3 received by the electrodes c_2 and c_3 was equal to the charge n_1 acquired by the electrode c_1. The centre of the stream was thus deflected through 2·5 mm. (half the width of the central plate) while the electrons travelled 4 cm. in the direction of the electric force.

The magnetic forces G required to deflect the centre of the stream through the angle $\tan^{-1} 0{\cdot}0625$ when the ions are moving under the electric force X are given by the curves (fig. 6). The different curves correspond to the different pressures of the air, which varied from 0·47 to 18·5 mm.

The velocity W under the electric force is given by the equation

$$GW/Z = \tan\theta = 0{\cdot}0625,$$

which expresses the condition that the direction of motion of the centre of the stream is along the resultant of the forces $Z \times e$ and $G \times We$. The latter force being small, the velocities W may be assumed to be the same as those in the experiments on the lateral diffusion when the forces Z were acting.

The values of W obtained from the formula $W = (Z/G) \times 0{\cdot}0625$ were found to depend on the ratio Z/p. This may be seen from the numbers in the last column of the table given in the preceding section. The values of W are expressed in centimetres per second, for the different forces and pressures.

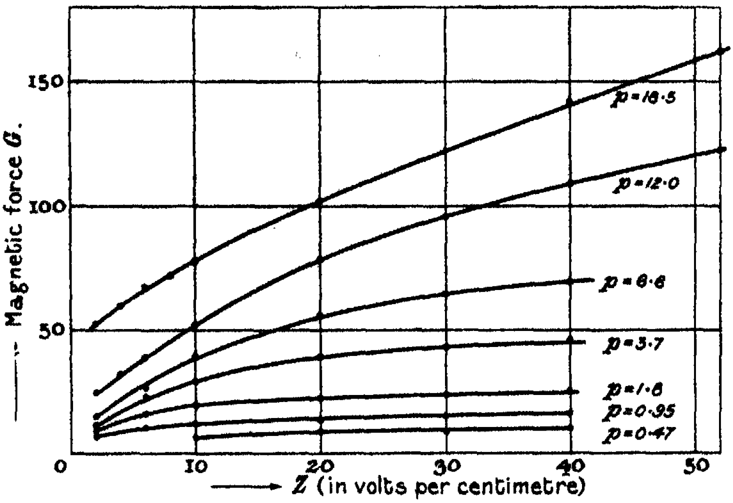


FIG. 6.

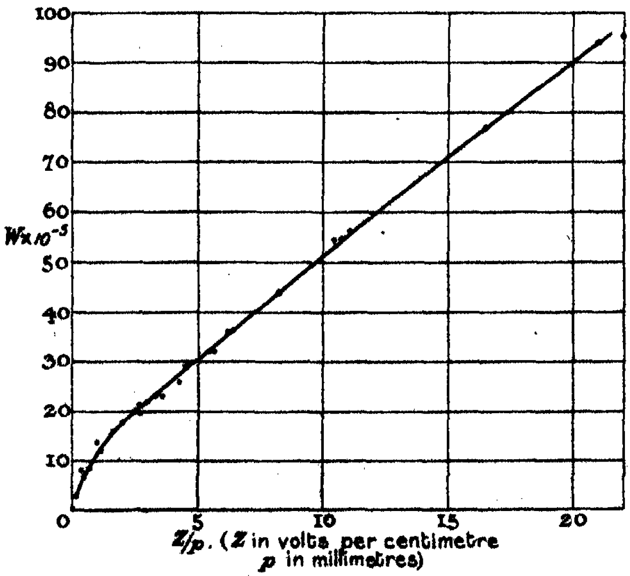


FIG. 7.

It follows that W is a function of Z/p and the velocities may be expressed by means of a single curve. The portion of the curve corresponding to values

of Z/p from 0·2 to 20 is given in fig. 7, and the remainder from $Z/p = 20$ to $Z/p = 200$ in fig. 8.

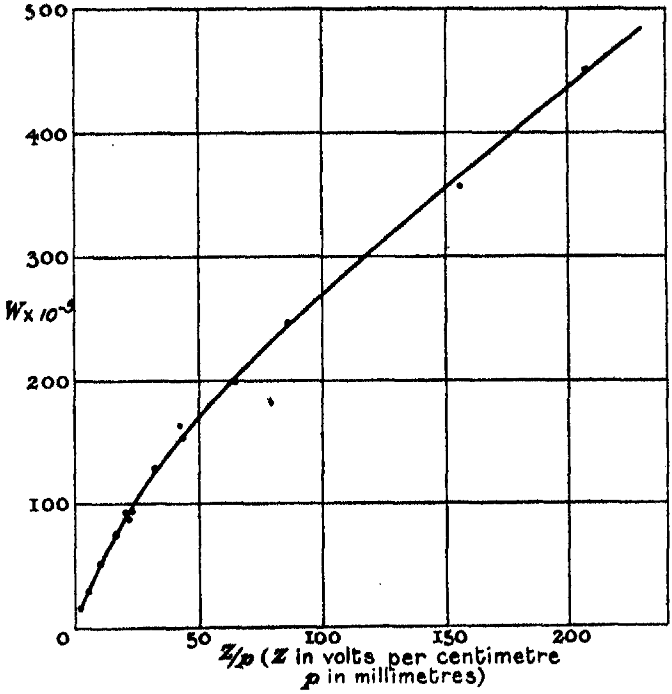


Fig. 8.

7. The following table gives a comparison between the velocity of agitation u and the velocity W in the direction of the electric force, in terms of Z/p:—

Z/p	0·2	0·5	1	2	5	10	20	50	100	150	200
$W \times 10^{-6}$	0·5	0·9	1·25	1·75	3·0	5·2	9·0	17·3	27	35	44
$u \times 10^{-6}$	16	24	34	47	62	67	75	101	127	145	156
$W \times u \times 10^{-12}$ ...	8·0	21	42	82	186	350	675	1740	3430	5100	6900
$e/m \times 10^{-17}$	5·1	5·8	5·8	5·4	4·4	3·9	3·6	3·9	3·8	3·6	3·8

The velocity W of a charged particle moving under an electric force is given approximately by the formula $W = (Ze/m)(l/u)$, when the mass m of the particle is small compared with that of a molecule of the gas, and the velocity of agitation u is large compared with W, l being the mean free path of the particle. When the pressure is constant l is also constant, and the velocity W is proportional to Z when m and u are independent of Z. In these cases m is constant, being the mass of an electron, but u increases with Z so that W does not increase in proportion to the force. The results of the experiments are thus in accordance with the theory, since W increases less rapidly than Z when p is constant; in fact, the

product $W \times u$ is approximately proportional to Z. The formula diminishes in accuracy as Z increases, since the velocity W approaches u.

In the above experiments a certain number of the ions that reach the electrodes c are generated by the collisions of the electrons with molecules of the gas. This does not affect the ratios of the charges acquired by the electrodes c_1, c_2, c_3, since the number of ions generated by collisions at each point of the gas is proportional to n, when the forces are not so large that the positive ions also generate others by collisions. The only effect of ionisation by collision in these experiments is to increase the charges n_1, n_2, and n_3, in the same proportion. With the larger pressures when Z/p is less than 20 the number generated by collisions is very small, but when the pressure is 0·47 mm. 60 per cent. of the ions are generated between the slit in B and the electrodes c when $Z = 40$ volts per centimetre.

8. The values of e/m for the charged particle may be deduced from the expressions for the velocity W, or the deflection θ, in terms of molecular quantities. The formulæ $W = (Ze/m)\,T$, and $\tan\theta = (He/m)\,T$, obtained under simplified conditions, only give approximate results, but a more complete investigation has been made by Langevin* of the rate of diffusion, and the velocity under an electric force for the case in which the collisions between the charged particle and the molecules are of the type that occurs between elastic spheres. The expression for the velocity W under these conditions is

$$W = \frac{3Ze}{8\sigma^2 N}\sqrt{\frac{h(m+m')}{\pi m m'}},$$

where m is the mass of the charged particle, m' that of a molecule of the gas, σ the sum of the radii of the particle and a molecule, N the number of molecules of the gas per cubic centimetre, and h three-fourths of the reciprocal of the kinetic energy of agitation of the particle or a molecule of the gas.

Since the mass of the electron is small compared with a molecule the ratio $(m+m')/mm'$ reduces to $1/m$, and $1/\pi\sigma^2 N$ is the mean free path l of the electron. The velocity W of an electron thus becomes

$$W = (Ze/m)(l/u)\,0{\cdot}815,$$

u being the velocity of agitation of the electron. The velocity W is therefore independent of the mass of the molecules and is proportional to $l/u = T$, the mean interval between collisions.

Langevin's formula is deduced on the hypothesis that the mean energy of agitation of the particle m is the same as that of a molecule of the gas. When the masses are of the same order of magnitude the interval between

* P. Langevin, 'Ann. de Chim. et de Phys.,' 1905, (8), vol. 5, p. 245.

collisions is a function of the velocities of both particles, but when the particle m is very small compared with m' the time T is determined by the velocity of agitation of the particle m. Hence in dealing with electrons the velocity u must be taken as the actual velocity of agitation, which exceeds that corresponding to a particle in thermal equilibrium with the molecules of the gas by the factor $\sqrt{k}$.

The value of e/m for the electrified particle may be obtained from the above equation by eliminating the quantity u. Thus

$$W^2 = (Z^2 e/m)(Ne/mNu^2)\, l^2 \times [0{\cdot}815]^2,$$

where $Ne = 1{\cdot}23 \times 10^{10}$ and $mNu^2 = 3k \times 10^6$. At a millimetre pressure the mean free path of a molecule of air may be taken as $7{\cdot}5 \times 10^{-6} \times 760$, so that the mean free path of an electron is $3{\cdot}2 \times 10^{-2}$ cm. Hence $lp = 3{\cdot}2 \times 10^{-2}$ and e/m is given by the formula

$$e/m = (Wp/Z)^2 (k/2{\cdot}8).$$

The values of e/m thus obtained from the determinations of W and k corresponding to the different values of Z/p are given in the above table (p. 345).

The numbers obtained for $e/m \times 10^{-17}$ do not differ very much from the value 5·3 found by the more accurate methods under conditions in which the effects of collisions between electrons and molecules may be neglected.

The differences between the values found for e/m for different values of Z/p are not entirely due to experimental errors, although the probable error in the final results is greater than that in the direct measurements, since the square of the velocity W is involved in the formula for e/m. The nature of the collisions between electrons and molecules may not resemble the collisions between elastic spheres to the same extent for different values of the velocity u.*

* Mr. F. B. Pidduck (p. 296, *supra*) has made a theoretical investigation of the motion of ions in gases; he shows that when the negative ions are in the electronic state their velocity of agitation may become abnormally large, and the above values of u and k may be explained on the hypothesis that the collisions between electrons and molecules are such as would occur between imperfectly elastic spheres.

Optical Investigation of Solidified Gases.—III. The Crystalline Properties of Chlorine and Bromine.

By Walter Wahl, Ph.D.

(Communicated by Sir James Dewar, F.R.S. Received February 26,—Read March 13, 1913.)

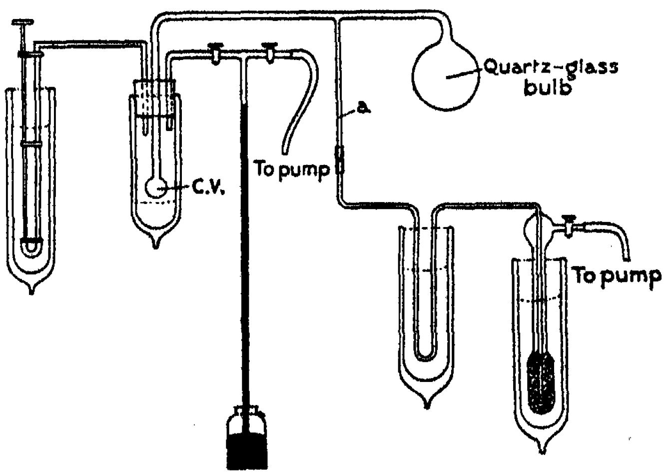
(From the Davy-Faraday Laboratory of the Royal Institution.)

Of the crystalline properties of the halogens only those of iodine are known. Of bromine, Arctowski has, at $-78°$, obtained red needles from a solution in carbon bisulphide,* but these have not been further examined. Dewar, quite early in his researches at low temperatures, stated that solid bromine gets much lighter in colour when it is cooled to the temperature of liquid hydrogen. Chlorine and fluorine† behave similarly; beyond this nothing is known as to the crystal properties of solid chlorine. Chlorine and bromine have, therefore, been investigated in continuation of the work described in 'Proc. Roy. Soc.,' A, vol. 87, p. 371, and A, vol. 88, p. 61.

Chlorine.

In order to obtain pure chlorine the gas was prepared from gold chloride and generated in the same piece of apparatus as was subsequently used for crystallising it. The device is shown in the figure.

The stem of a quartz-glass crystallisation vessel (C.V.) of the kind



* Arctowski, 'Zeitschrift für Anorgan. Chemie,' 1895, vol. 10, p. 25.

† Moissan and Dewar, 'Comptes Rendus,' 1903, vol. 136, p. 642.

previously described was first passed through a rubber stopcock fitting into a small vacuum vessel, and to this stem was then sealed a kind of small fractionating bulb of quartz-glass (see fig.), the connecting tube being bent at right angles. The bulb itself had a capacity of about 50 c.c. About 15 grains of gold chloride were brought into the bulb, and by means of a short piece of rubber pressure-tubing the side-tube was then connected to a **U**-tube, which again was connected to a charcoal bulb (right-hand portion of figure). The **U**-tube and the charcoal bulb were then immersed in liquid air and the interior of the entire quartz-glass apparatus was thus dried in high vacuum for a considerable time. The quartz-glass bulb containing the gold chloride was subsequently heated in an oil bath, the temperature being raised gradually up to 125°. In this high vacuum the gold chloride began to give off some chlorine at about 100°, and at 125° the chlorine was so freely given off that the heating was discontinued. The moisture and HCl, resulting from the action of chlorine on the moisture, together with the quantity of chlorine already given off by the gold chloride and any products possibly arising by the action of the chlorine on the rubber connection between quartz and glass, were in this way condensed and solidified in the **U**-tube immersed in liquid air. The quartz-glass bulb was then allowed to cool, the charcoal vacuum being maintained all the time, and the quartz-glass apparatus sealed off at *a* (see fig.) by an oxygen blowpipe. A syphon and a tube connected with a mercury barometer valve, and through this to the vacuum tank of the laboratory, were then inserted into the rubber stopcock, and this fixed into the vacuum vessel (left portion of figure).

The liquefaction and solidification of the chlorine was effected in the following manner. The crystallisation vessel was first cooled to some extent by admitting a small quantity of liquid air into the vacuum vessel and letting it boil off. The quartz-glass bulb containing the gold chloride was then gently heated with a burning match, the heat from three or four matches being quite sufficient to generate the small quantity of chlorine needed to fill the minute space between the discs of the crystallisation vessel and the lower part of its stem.

When the crystallisation vessel had been cooled strongly before the gold chloride was heated, the chlorine was condensed in the form of quite minute isometric crystals on the walls of the discs of the crystallisation vessel. These small crystals were very sharp and perfect, showed very brilliant light reflexes and seemed to possess a high refractive index. Between crossed nicols they showed bright interference-colours and are thus double-refracting. Owing to their small size it was not possible to make out anything as to their crystalline form.

If the crystallisation vessel is slowly cooled while the chlorine is generated, this can easily be condensed as a liquid and subsequently crystallised by further cooling. It then solidifies in the form of very beautiful crystalline growth-structures. These grow chiefly in the direction of a principal axis, simultaneously sending out branches to each side, at an angle of about 40° to 50° with the principal axis. The space between the branches of the growth-structure is filled up, in a later stage of the crystallisation process, and in this way homogeneous crystal fields result.

When cooled further, a distinct cleavage parallel to the principal axis of the growth-structure is formed. In spite of the thinness of the crystal film between the discs of the crystallisation vessel, the crystal fields appear distinctly pale yellow in colour. The polarised light travelling parallel to the cleavage and principal axis is more strongly absorbed, and the transmitted light is of a deeper yellow, with a greenish tint, than is the polarised light passing in directions at right angles to the principal axis. There is a slight difference in the degree of absorption in the two directions at right angles to the principal axis, but in such a thin crystal layer no difference in colour is noticeable between these directions.

The crystallised chlorine is, in sections both parallel and at right angles to the principal axis, strongly double-refracting. The extinction between crossed nicols is parallel to the principal axis, as indicated by the cleavage. Chlorine thus belongs to the *orthorhombic system.*

When the crystallised chlorine is further cooled the cleavage is further developed, but no polymorphic change has been observed at temperatures between that of the melting point and that of liquid air. The absorption in the direction parallel to the principal axis gradually diminishes when the preparation is cooled, and at liquid-air temperatures scarcely any difference in colour in different directions is noticeable, the crystals appearing quite pale, scarcely coloured at all.

Bromine.

Some preliminary tests were made with ordinary bromine, brought directly into the stem of a crystallisation vessel and then sucked into the narrow space between the quartz-glass discs by alternately gently heating and cooling these. As it was found that solid bromine is quite sufficiently transparent in such thin layers, a small sample of pure dry bromine was investigated in the piece of apparatus used for the investigation of chlorine.

A quantity of pure bromine ("Kahlbaum") and some phosphorus pentoxide were brought into a small glass bulb provided with two tube-necks. One of these was drawn out so as to fit into the open end of the

small side-tube, *a*, of the quartz-glass apparatus. The joint was made secure by slipping a piece of rubber pressure-tubing over it. This acted as a spring, pressing the parts together. The other tube of the bulb was connected with a U-tube immersed in liquid air, and this with a charcoal bulb.

The bromine contained in the glass bulb was frozen by applying to it a wad of cotton-wool drenched in liquid air. The apparatus was then exhausted by means of the charcoal and sealed off between the glass bulb containing the bromine and phosphorus pentoxide and the U-tube. The quartz-glass apparatus and the bromine were in this way left to dry in vacuum over phosphorus pentoxide. Subsequently, part of the bromine, about 1 c.c., was sublimated over into the quartz-glass bulb by cooling this with liquid air. The quartz-glass apparatus was then sealed off. The bromine was sublimated over into the crystallisation vessel by cooling this with liquid air, and investigated as described in the previous cases.

Crystallised bromine is very similar to crystallised chlorine, only all the properties appear more pronounced. The most striking feature is the strong pleochroism. The crystal grains and fields show a tendency to develop in prismatic forms, and a prismatic cleavage is very distinct. There is also an indication of a basal cleavage, but this becomes distinct only at low temperatures. The prismatic cleavage angle is about 70°. The double refraction is strong, and the extinction is parallel to the cleavage—that is, to the principal axis—and in sections at right angles to the principal axis it is parallel to the line bisecting the cleavage angle.

The absorption is: *dark brownish red* in the direction of the prism axis, *yellowish red* in the direction of a line bisecting the smaller prism-angle, and *pale yellowish green* in the direction of the line bisecting the larger prism-angle. On cooling, the strong absorption in the direction parallel to the prism-axis rapidly diminishes, and at the same time the transmitted light gradually becomes more yellowish red, and subsequently yellow. Also, in the direction of yellowish-red absorption a similar change takes place, resulting in a pale yellow colour at liquid-air temperature. In the case of the third principal direction of absorption it is difficult to observe if a change takes place or not, as the colour is already so light at temperatures close to the melting point.

The change in colour of solid bromine from brownish red, nearly black as it appears near the melting point, to very pale yellow at the temperature of liquid air, and subsequently to quite a pale tint at the temperature of liquid hydrogen, as described by Sir James Dewar, is thus principally due to a gradual disappearance of the strong trichroism which it possesses at temperatures close to the melting point, the crystals assuming at low temperatur

more or less the colour they exhibit at high temperature in one certain crystallographic direction. An alteration of the pleochroism with change of the temperature has been observed by Kirchhoff in the case of green tourmaline.*

The above optical characters, as well as the cleavage, show that bromine crystallises in the *orthorhombic system*. No polymorphic change has been observed in the temperature range comprised between the melting point and that of liquid air.

The Relations between the Crystalline Properties of Chlorine, Bromine, and Iodine.

Iodine has been investigated crystallographically by Mitscherlich, who found that it crystallises in the rhombic system and with a prism-angle of 67° 12'.† Recently, v. Fedorow, investigating iodine crystals that had sublimated on the asbestos stopper of a reagent bottle, found that these consisted both of the ordinary rhombic tablets and of prisms which belong to the monoclinic system.‡ Both kinds of crystals are very similar in colour and general appearance. Iodine is thus dimorphic. Both forms can be obtained from solutions in CS_2, $CHCl_3$, alcohol, and petrol-ether, the monoclinic being formed when the solution is very rapidly evaporated, the ordinary rhombic form when the solution is allowed to evaporate slowly. V. Kurbatoff found, in addition, that on sublimation of iodine the ordinary form is produced when the temperature is above +46·5°, and that monoclinic prisms are formed when the temperature at which the sublimation is carried out is lower.§

With regard to the optical properties of iodine hardly anything is known. Jörgensen states, however, that extremely thin dendritic crystals, obtained on a glass plate by the evaporation of an iodine solution in ether, act as polarisers ("artificial tourmalines") and appear in polarised light either black or light brown, according to the direction of their principal elongation with reference to the polarisation plane.‖ Sufficiently thin crystal-layers can also be obtained simply by melting a small crystal of iodine between two glass plates and squeezing these firmly together while the preparation is cooling and the iodine crystallising. I am able to corroborate the statements of Jörgensen and to add that total absorption takes place when the direction

* G. Kirchhoff, 'Pogg. Ann.,' 1860, vol. 109, p. 299.

† See v. Groth, 'Chemische Krystallographie,' vol. 1, p. 33.

‡ v. Fedorow, 'Bull. Acad. Petersburg,' 1907, (5), vol. 22, p. 287.

§ v. Kurbatoff, 'Zeitschrift f. Anorg. Chemie,' vol. 56, p. 230.

‖ S. M. Jörgensen, 'Berichte Chem. Ges. Berlin,' 1869, vol. 2, p. 465.

of the principal axis is parallel to the plane of polarisation. The light transmitted at right angles to the principal axis is, in these extremely thin growth-structures, either light reddish-brown, or light leather-brown, there being no great difference of absorption visible between these directions, probably on account of the thinness of the crystal-layer. It was further found that the colours appeared considerably paler in the direction at right angles to the principal axis, when the preparation was cooled in liquid air. The absorption in the direction parallel to the principal axis remains, however, even at low temperature, strong enough to extinguish the polarised light totally in this direction.

No transition into a monoclinic form takes place when the rhombic growth-structures are cooled to about $-180°$, as is clearly seen from their behaviour in polarised light. It seems, therefore, not probable that the monoclinic form is the one stable at low temperatures, the rhombic at high temperatures, the transition point being $+46{\cdot}5°$, as suggested by Kurbatoff. The ordinary rhombic modification of iodine is probably the modification stable at all temperatures, the monoclinic prisms belonging to a monotropic form with a marked temperature-limit of formation, and apparently low velocity of transition at ordinary temperature. Their opaqueness and metallic character render it impossible to know if the monoclinic crystals investigated by v. Fedorow and Kurbatoff were pseudomorphosed or not. The formation of the monoclinic form by rapid evaporation of solutions indicates also that it is a sporadically formed monotropic modification, and that a transition-point between the two modifications does not exist.

If we compare crystallised chlorine, bromine, and iodine with each other, we thus find that all three elements are rhombic. From the investigation of the melting points of the systems chlorine-bromine, chlorine-iodine,* and bromine-iodine,† we are enabled to conclude that they form a continuous series of mixed crystals, and may thus be regarded as perfectly isomorphic. The pleochroism of the three members of the series is of particular interest, as it occurs in all members of the group, and its strength and character—like the other physical and chemical characters of the group—change and increase as the atomic weight increases. It is, however, specially remarkable that the colour in the direction of principal absorption in chlorine should be so closely the same as the colour in the direction of weakest absorption in bromine, and that the colour of strongest absorption in bromine should be about the same—as far as determination is possible—as that of weakest absorption in iodine.

* B. J. Karsten, 'Zeitschr. f. Anorg. Chemie,' 1907, vol. 53, p. 365.

† Meerum Terwogt, 'Zeitschr. f. Anorg. Chemie,' 1905, vol. 47, p. 203.

The Relation between the Crystal-Symmetry of the Simpler Organic Compounds and their Molecular Constitution.—Part I.

By Walter Wahl, Ph.D.

(Communicated by Sir James Dewar, F.R.S. Received March 21,—Read April 17, 1913.)

(From the Davy-Faraday Laboratory of the Royal Institution.)

Introduction.

Certain relations between the chemical composition of bodies and their crystalline forms indicate that the crystallographic properties depend in a simple way on the chemical constitution. There are three distinct relations which principally point towards such a connection.

1. *The Isomorphism* shows that similarly constituted compounds, even of a very complicated chemical composition, crystallise in a very similar way when certain atoms in the molecule are replaced by chemically related atoms. There are probably few subjects in the whole field of chemistry upon which so much separate evidence has been collected. As a result of all this research upon isomorphic relationship and isomorphic series, from that of Mitscherlich up to the recent work of Tutton, it may be concluded with a great amount of certainty that to a definite molecular edifice belongs a certain crystalline edifice. In consequence, the replacement of one or several atoms in such a molecular structure by atoms chemically closely related does not imply more than a slight alteration in the crystal form.

2. *The Morphotropy* (in the sense of v. Groth) implies that, if a certain atom or group in a large molecular-complex is replaced by another group, a definite alteration of the crystal-form in a certain crystallographic direction may take place. This shows that changes in the constitution of a molecule are accompanied by corresponding changes in the crystal-form of the body, and thus also serves to establish the existence of a general relationship between molecular and crystallographical build.

3. *The Enantiomorphism.*—All the substances which in the liquid state or in solution exhibit the property of rotating the plane of polarisation, crystallise as two "enantiomorphic" forms (Law of Pasteur). When the molecular edifice shows a lack of symmetry, as a result of which right- and left-handed modifications exist, the two being mirror-images of each other, a similar lack of symmetry, accompanied by the occurrence of crystals which form mirror-

images of each other, also exists between its crystallisation products. Enantiomorphism, therefore, may be regarded as a proof of the existence of a general relationship between molecular and crystallographical properties.

There are, however, at present few data which may be used to correlate the evidence as established separately by isomorphism, morphotropy, and enantiomorphism. Most of the work on isomorphism has been done on salts and double salts of a complicated nature; the investigations on morphotropy on organic bodies with a large molecule, mostly those of the aromatic series; and in those cases in which the crystal-forms of optically active organic bodies have been investigated the molecules are nearly all of great complexity.

The circumstance that nearly all organic bodies of simple chemical composition at ordinary temperatures are gaseous or liquid, and their crystalline properties therefore hitherto unknown, must, of course, be regarded as one of the principal difficulties to be overcome in establishing the facts governing the relationship between their molecular constitution and crystal-form. As an illustration of how little is really known with regard to the crystalline properties of the simpler organic compounds, it may be noted that in the 'Chemical Crystallography,' edited by von Groth (of which the recently issued third volume contains all crystallographic data hitherto obtained concerning aliphatic and hydro-aromatic compounds), only three methane derivatives are quoted (carbon tetrabromide, iodoform, and di-isonitramido-methane-dimethylether) which have not the character of salts containing metallic atoms, such as, for instance, the formates.

In connection with the recent investigations by the author on the crystalline properties of the elements gaseous at ordinary temperature, which have been described in the 'Proceedings of the Royal Society,'* some observations were made on certain of the simpler organic compounds of low melting point. As some interesting observations were made on the relations between the crystalline properties of similarly constituted compounds, and also on the occurrence of polymorphic modifications, the investigation was extended to a larger number of the simpler organic compounds. The experimental data concerning the *aliphatic hydrocarbons* are presented in this paper. The results with regard to the halogen- and nitro-derivatives of methane, together with the general conclusions to be drawn from all these experimental data, will be given in a further communication.

* W. Wahl, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 371; 1913, A, vol. 88, p. 61; 1913, A, vol. 88, Feb. 26.

Experimental Investigation.

In investigating the bodies, gaseous or liquid, at ordinary temperatures, practically the same methods were employed as have been described in 'Proc. Roy. Soc.,' A, vol. 87, pp. 371–374 and 376–378. The solid bodies were brought into the stem of the crystallisation vessel, melted and sucked into the narrow space between the polished quartz-glass plates, and their crystallisation and behaviour on cooling to liquid-air temperature investigated as in the case of the liquids.

As pointed out in the case of methane, it is necessary to use the substances to be investigated in a very high state of purity in order to be able to study properly their manner of crystallising. All the gases have therefore been fractionated by using liquid air or solid carbonic acid to condense them, a middle fraction being collected in a small glass gasometer over distilled mercury and used for these investigations. The liquids were in most cases distilled immediately before investigation, a Young's still-head in three sections being employed. The solids were in some instances purified by sublimation in a charcoal-vacuum in a way similar to that described in the case of bromine.*

Methane.—Methane crystallises in the regular system. The account of the investigation of methane has been published in 'Proc. Roy. Soc.', A, vol. 87, p. 377. It is therefore sufficient to refer to that paper for details.

Ethane.—Ethane was prepared in the way described by Frankland,† by reducing ethyl iodide with coppered zinc. The gas was passed through potassium hydroxide solution and through concentrated sulphuric acid, and then condensed and again boiled off and collected over water in a glass gasometer of the type designed by Bunsen, and of a capacity of about $1\frac{1}{2}$ litres. From here it was passed, for final purification, through a series of small wash-bottles containing bromine under water, a solution of potassium hydroxide, and concentrated sulphuric acid. From the wash-bottles the gas passed through a tube fitted with a stopcock into a condensing vessel of the wash-bottle type, where it was condensed by cooling with liquid air. The outlet tube of the condensing vessel was provided with a two-way stopcock leading to a barometer mercury-valve and to a T-piece, which again was in communication through the one branch with a mercury-gasometer of about 100 c.c. capacity and through the other branch, which was provided with a stopcock, with a large Fleuss pump. When all the gas from the large gasometer condensable at liquid-air temperature had been condensed, after having passed through

* 'Roy. Soc. Proc.,' A, vol. 88, Feb. 26.

† E. Frankland, 'Liebig's Ann.,' vol. 71, p. 203; vol. 85, p. 360; vol. 95, p. 53; and 'Chem. Soc. Journ.,' 1885, vol. 47, p. 236.

the absorption bottles, the stopcock between these and the condensation vessel was closed. The ethane in the condensation vessel remained liquid in spite of this being immersed in liquid air, which shows that ethane prepared in this way cannot be obtained in a pure state by simply passing it through the absorbing agents mentioned above, and even condensing it once. When the condensation vessel, however, was evacuated by means of the Fleuss pump, the liquid solidified.

It is probable that the ethane prepared in the above manner contains some methane, but it may also be that when it is condensed in presence of hydrogen, or perhaps also of air, it dissolves a sufficient quantity of the lighter gas to remain liquid at $-180°$. These circumstances account for the statement concerning ethane, often to be found in the literature, that its melting point lies below the boiling point of liquid air. All the lower members of the methane series behave in a very similar way, that is, they remain liquid at temperatures very much below their true melting point if purified only by passing through bromine, and condensed for the first time from the gaseous reaction products mixed with air. By the evacuation following upon the solidification the lighter volatile products were pumped away. The solid was then melted and the liquid was allowed to boil off gradually from the condensation vessel, the first portions being boiled off through the mercury barometer valve. A further small portion was then used to wash out the tubes and connections with the mercury gasholder, these being subsequently evacuated. About 100 c.c. of the middle fraction of the ethane were then collected into the mercury gasholder.

The ethane purified in this way was used for the crystallisation investigations. It crystallises very readily in fern-like broad blades, growing rapidly in one principal direction. If rapidly cooled, the liquid can be supercooled and becomes at about $-200°$ a glass traversed by numerous cracks. When the temperature is then allowed to rise spherulitic crystallisation sets in. If the surface of the liquid air in the Dewar-vessel surrounding the crystallisation vessel is kept about 1 cm. below this, it is easy to crystallise and melt the ethane alternately by simply turning on and off the exhaust on the liquid air.

The crystal-fields of ethane show no cleavage at a temperature close to that of the melting point. When the preparation is further cooled by evacuating the liquid air a very marked cleavage in two directions is developed. The double-refraction varies very much in different directions, the maximum value, however, not being much higher than that of quartz. Crystal fields occur also which remain isotropic when the nicols are revolved. The direction of extinction in the double-refracting sections bisects the angle

between the two cleavage-directions. Judging from the occurrence of isotropic sections, and from the cleavage, which must be regarded as rhombohedral, ethane is hexagonal.

Propane.—Propane was prepared in a similar manner to ethane by reducing isopropyl iodide with coppered zinc. Judging from the fact that nearly half the volume of the reaction product was absorbed when passed through bromine, a very large proportion of olefinic hydrocarbons are formed in this case. The fractionation was effected in the same way as described in the case of ethane.

When cooled in the vapour of evaporating liquid air the liquid propane does not crystallise. If liquid air is admitted through the syphon until the crystallisation vessel is partly submerged in the liquid air, and the temperature is still further lowered by exhausting the liquid air, crystallisation after some time sets in. The liquid is at this temperature not yet supercooled sufficiently to become stiff or glassy; the crystalline phase, however, grows very slowly and spreads in most cases in one single homogeneous crystal-field over the whole field of the microscope. By variation of the exhaust, that is the temperature of the liquid air, a growth in the form of prismatic needles can be obtained at the fringe of the crystal field. This crystalline form of propane is strongly double-refracting and apparently rhombic.

When the exhaust on the liquid air is turned off and the temperature allowed to rise, a transition into another form takes place. This form, which appears to be stable at higher temperatures, grows very slowly in the other modification, but in precisely the same way as crystals grow in a liquid. This crystalline form is also strongly double-refracting, and either rhombic or monoclinic. When the temperature rises further it begins to melt, and if only a portion is melted and the preparation then again cooled, recrystallisation takes place in the form of very narrow, sharp needles, projecting from the margin of the crystal-field into the molten mass. If the crystals are, however, totally melted, supercooling of the liquid invariably takes place on cooling, and the crystal modification formed spontaneously in the supercooled liquid is always the form stable at lower temperatures. Thus in propane we meet with a polymorphic substance which behaves in a similar way to sulphur—and in a certain sense to oxygen—in this respect, that the modification stable at low temperature is formed directly by the crystallisation of the supercooled liquid, *i.e.*, in the case of oxygen, the glassy liquid. In all three cases the transition-point temperature lies only slightly below that of the melting point, and all three substances strongly tend to become supercooled, and also show little velocity of crystallisation in the case of the modification stable at higher temperature.

Trimethyl-methane (Tertiary Butane).—Trimethyl-methane was prepared from tertiary butyl iodide in a way similar to that described in the case of the preparation of ethane and propane, and the reaction product treated as described in the case of ethane. The gas obtained after the first condensation was absorbed, however, to the extent of about 80 per cent. when passed through bromine, showing that principally olefinic hydrocarbons are formed in this case.

Trimethyl-methane crystallises very beautifully in large crystal-fields and prismatic columns. These are strongly double-refracting. On further cooling with liquid air a very regular cleavage in one direction is developed. The extinction is parallel to this cleavage direction. It is therefore possible that trimethyl-methane is rhombic, but it may also be that the crystal-fields are always developed parallel to one and the same crystal face, as, remarkably enough, the interference colour in all cases was the same. These observations, therefore, cannot be regarded as conclusively determining to which crystal system trimethyl-methane belongs.

Tetramethyl-methane (Quaternary Pentane).—Tetramethyl-methane was prepared according to Lwow,* *i.e.* by the action of a calculated quantity of zinc-methyl on tertiary butyl iodide. It was found that the reaction is very treacherous, and it is not safe to work with more than quite small quantities. If the iodide is not sufficiently cooled while the zinc-methyl is added, the reaction product is, for the greater part, absorbed when passed through bromine. If more strongly cooled, reaction does not take place at all, and, when the mixture of the iodide and zinc-methyl is allowed to get gradually warmer, the reaction does not commence gradually, but sets in quite suddenly and a most violent explosion takes place. The raw gas was purified by passing successively through bromine, caustic potash solution, and concentrated sulphuric acid, and was then frozen and subsequently fractionated.

Lwow states that the tetramethyl-methane crystallises in similar grille structures to ammonium chloride.

Investigated in the same manner as the substances described above tetramethyl-methane has been found to crystallise in very beautifully developed cubical growth-structures, which are later filled up, and become homogeneous crystal-fields. These are absolutely isotropic between crossed nicols. When the preparation is cooled, a cubical cleavage is first developed, and at low temperature a transition into another modification of low double-refraction takes place, which, to judge by its optical characters, is probably tetragonal.

* Lwow, 'Zeitschr. f. Chemie,' 1870, vol. 6, p. 520; and 1871, vol. 7, p. 257.

Normal Butane.—Normal butyl iodide is not acted upon at ordinary temperature by coppered zinc and alcohol. The reaction product obtained at higher temperature does not seemingly contain any appreciable amount of *n*-butane. Lebeau has described a method for the reduction of alcoholic iodides by sodium dissolved in an excess of liquid ammonia. He claims this method to be generally applicable to the synthesis of saturated aliphatic hydrocarbons. I have tried to prepare the *n*-butane as described by Lebeau.* The action of the deep blue sodium solution on the iodide takes place readily, but instead of a reduction taking place the reaction proceeds according to the Wurtz reaction, that is sodium iodide and octane are formed. Only an insignificant quantity of gaseous reaction products was formed, and a slight smell of amines was noticeable.† Finally, the Grignard reaction was tried and gave a good yield of the hydrocarbon. This was then purified by condensation, passing through bromine and solidification, followed by fractionating.

n-Butane crystallises readily, and large crystal-fields are formed. Both double-refracting sections showing parallel extinction and isotropic sections are observed. The uniaxial character of the crystals in this case was also confirmed by observation in convergent polarised light. *n*-Butane must thus be regarded as hexagonal. At a temperature close to that of liquid air, boiling at ordinary pressure, this modification changes into another which exhibits a stronger double refraction and is rhombic. On heating the reverse change into the hexagonal modification takes place.

Normal Pentane (Kahlbaum's, from petroleum).—The commercial product did not crystallise, and it was not possible to obtain by fractionation a quite homogeneously crystallising preparation. Only a certain middle fraction crystallised fairly well, and this was further fractionated and investigated. On cooling, it at first became supercooled, but could be brought to crystallise by rubbing the inner wall of the stem of the crystallisation vessel with a metal wire. It at first crystallises in the form of spherulites, but can be recrystallised, and is then obtained as long needles and prismatic fields of parallel extinction, and low double-refraction, which belong to the rhombic system. Crystalline growth-structures, very similar to those of olivine, as

* P. Lebeau, 'Bull. Soc. Min.,' [3], vol. 33, p. 1089, and 'Bull. Acad. Belgique,' [3], 1908, vol. 46, p. 300.

† The reaction occurred twice in this way; I have, however, not had the time to study the case further. Quite recently E. Chablay ('Compt. Rend.,' January 27, 1913) stated that the hydrocarbons of the ethylene-series may also be obtained in a similar way. Remarkably enough the reaction between sodium dissolved in liquid NH_3 and the alcoholic iodides thus seems to be able to proceed in three different ways, in each case giving good yields. The conditions under which the one or the other product is obtained are, however, not known.

seen in basaltic rocks, were also observed. A small quantity of the liquid did not crystallise at all, but became glassy at low temperature.

Normal Hexane (Kahlbaum's, from propyl iodide).—*n*-Hexane crystallises in needle-shaped prisms which exhibit extinction angles of very different degree. The double-refraction is moderately high. At liquid air temperature a very distinct longitudinal cleavage is developed. No polymorphic change takes place above $-200°$, but at low temperature sparse twinning lamellæ are formed, lying at an angle of about 80° to the prism axis; *n*-hexane is thus monoclinic or triclinic, probably monoclinic.

Normal Heptane (Kahlbaum's, from petroleum).—The commercial product does not crystallise well, and a homogeneous preparation could no more be obtained in this case than in the case of *n*-pentane. The principal crystallisation product of the middle fractions consisted of long monoclinic or triclinic needles.

Normal Octane (Kahlbaum's, from *n*-butyl iodide).—*n*-Octane crystallises well and in large prismatic columns of moderately high double-refraction. It is monoclinic or triclinic. No polymorphic transition has been observed above $-200°$.

Ammonium Ferrous Sulphate and its Alkali-metal Isomorphs.

By A. E. H. Tutton, D.Sc., M.A., F.R.S.

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Ammonium ferrous sulphate, $(NH_4)_2Fe(SO_4)_2.6H_2O$, although one of the commonest double salts in everyday laboratory use, and noted for its excellent, comparatively stable, clearly transparent, pale greenish-blue crystals, has never yet been subjected to a thorough crystallographic and optical study. Since the year 1859, when a few of its principal angles were measured by Murmann and Rotter,* and an approximate idea of its optical properties for red, yellow, and green light of no specific wave-lengths briefly indicated, just adequately to confirm that the salt belongs to the monoclinic series of double sulphates crystallising with $6H_2O$, no accurate measurements have been made. The substance has, however, formed the subject of several special researches from a different point of view, such as those of von Hauer† on the parallel growths of this salt on crystals of other salts of the series, of

* Murmann and Rotter, 'Sitzungsber. d. Akad. d. Wiss. Wien,' 1859, vol. 34, p. 153.

† K. von Hauer, 1860, *ibid.*, vol. 39, p. 611.

Baumhauer* concerning the etch-figures produced on the various faces of the crystals by a small quantity of water, by St. Meyer† on the nature of the crystals deposited under the influence of a magnetic field, by Wulff‡ on the different rapidity of growth of the different crystal faces, and by von Fedorow§ concerning the correct setting of the crystals for descriptive purposes. But this salt was not included in the well-known series of optical investigations of Topsöe and Christiansen in 1874–5, nor the later one of Perrot, and has not been hitherto included by the author in his detailed investigation of the salts of this isomorphous series. This omission is now, however, removed by this communication.

Morphology.

In common with the whole of the salts of the large isomorphous series, $R_2M\left\{\begin{matrix} S \\ SeO_4 \\ Cr \end{matrix}\right\}_2.6H_2O$, ammonium ferrous sulphate crystallises in the monoclinic system with full holohedral symmetry. That the class is the holohedral one (Class 5, holohedral-prismatic) was proved by Baumhauer as the result of his investigation of the etch-figures afforded by water (see figs. 8 and 9, on pp. 371 and 372).

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—$a : b : c = 0{\cdot}7377 : 1 : 0{\cdot}4960$. Values of Murmann and Rotter, $0{\cdot}7466 : 1 : 0{\cdot}4950$.

Axial Angle.—$\beta = 106° \; 50'$. Value of Murmann and Rotter, $106° \; 48'$.

Forms observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $p'''\{130\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o\{111\}$, $o'\{\bar{1}11\}$.

Habit.—Chiefly tabular parallel to $r'\{\bar{2}01\}$; frequently elongated along the edge $[20\bar{1} : 010]$, or $[20\bar{1} : 110]$; occasionally with $c\{001\}$, $p\{110\}$, $r'\{\bar{2}01\}$, and $q\{011\}$ more or less equally developed. Murmann and Rotter also observed a tabular form parallel to $r'\{\bar{2}01\}$, prolongation along the edge $[201 : 1\bar{1}0]$, and predominating development of $c\{001\}$, $p\{110\}$, and $r'\{\bar{2}01\}$, with subordinated $q\{011\}$, $o'\{\bar{1}11\}$, and $b\{010\}$, the latter type being shown in fig. 1.

The salt is thus characterised by predominating development of the pair of parallel faces of the form $r'\{\bar{2}01\}$, which is usually only a subordinate one for the series in general. Three typical crystals measured by the author are represented in figs. 2, 3, and 4. The types 3 and 4 are clearly tabular

* H. Baumhauer, 'Pogg. Ann. d. Phys.,' 1873, vol. 150, p. 619.

† St. Meyer, 'Sitzungsber. d. Akad. d. Wiss. Wien,' 1899, vol. 108 (IIA), p. 513.

‡ G. Wulff, 'Zeitschr. für Kryst.,' 1901, vol. 34, p. 486.

§ E. von Fedorow, 1909, *ibid.*, vol. 46, p. 258.

parallel $r'\{\bar{2}01\}$, and type 4 is only distinguished from type 3 by the larger development of the faces of the basal plane $c\{001\}$ and clinodome $q\{011\}$. The next best developed faces are those of the primary prism $p\{110\}$ and of the hemipyramid $o'\{\bar{1}11\}$, which are present to about the same extent, modifying the edges of $r'\{\bar{2}01\}$. The two faces of the clinopinakoid $b\{010\}$ are usually present, and in type 2 the crystal is elongated in the direction of

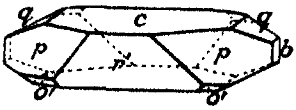


Fig. 1.

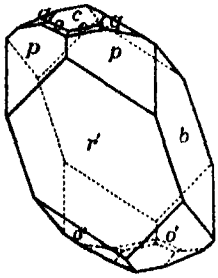


Fig. 2.

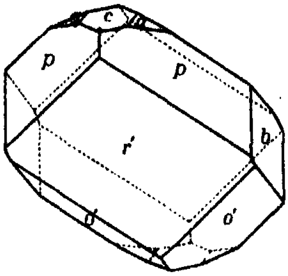


Fig. 3.

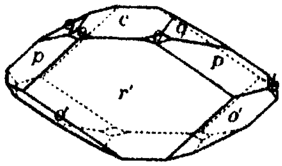


Fig. 4.

Typical Crystals of Ammonium Ferrous Sulphate.

the edge br', so that the b-faces are long and narrow. Good little faces of the hemipyramid $o\{111\}$ were present on two of the measured crystals, and very narrow faces of $p'''\{130\}$ were discovered on one crystal, but their signal-images were neither sufficiently clear nor adequately free from diffraction to be of use other than for identification purposes.

Twelve excellent crystals were measured, of which ten were small and very perfectly formed, while two were larger, but yet gave excellent single images of the Websky signal. The crystals were selected from four different crops, which had been grown under ideal conditions of slow deposition and freedom from disturbance. These measured crystals in general yielded splendidly sharp and clear images of the signal, as will be obvious from the excellent agreement between the measured and calculated angles in the following table of angles. Other crops were considerably influenced by striation of the c- and p-faces, an occurrence which has been shown to be general throughout this series of double salts.

Table of Angles.—The following table presents the results of the measurements and calculations. The values of Murmann and Rotter, and also some earlier ones of Kopp,* are included in the last two columns.

* Cited in Rammelsberg, 'Handbuch d. kryst. phys. Chemie,' Leipzig, 1881, vol. 1, p 460.

Interfacial Angles of Ammonium Ferrous Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of	
						M. & R.	Kopp.
		° ′ ° ′	° ′	° ′	′	° ′	° ′
ac = $(100):(001)$	—	—	—	73 10	—		73 12
as = $(100):(101)$	—	—	—	44 52	—		
sc = $(101):(001)$	—	—	—	28 18	—		
cr′ = $(001):(\bar{2}01)$	13	64 26– 64 42	64 35	64 36	1	64 5	
cs′ = $(001):(\bar{1}01)$	—	—	—	38 36	—		
s′r′ = $(\bar{1}01):(\bar{2}01)$	—	—	—	26 0	—		
r′a = $(\bar{2}01):(\bar{1}00)$	—	—	—	42 14	—		
r′c = $(\bar{2}01):(00\bar{1})$	14	115 15–115 37	115 26	115 24	2		
ap = $(100):(110)$	—	—	—	35 13	—		
pp′ = $(110):(120)$	—	—	—	19 28	—		
p′b = $(120):(010)$	—	—	—	35 19	—		
pp‴ = $(110):(130)$	—	—	—	29 30	—		
p‴b = $(130):(010)$	—	—	—	25 17	—		
pb = $(110):(010)$	28	54 40– 54 55	54 47	*	—	54 29	
pp = $(110):(1\bar{1}0)$	13	70 23– 70 31	70 26	70 26	0	71 7	71 30
cq = $(001):(011)$	22	25 12– 25 34	25 24	*	—	25 16	25 21
qb = $(011):(010)$	16	64 27– 64 41	64 36	64 36	0		
ao = $(100):(111)$	—	—	—	48 1	—		
oq = $(111):(011)$	1	—	26 55	26 49	6		
aq = $(100):(011)$	—	—	—	74 50	—		
qo′ = $(011):(\bar{1}11)$	3	34 45– 34 56	34 51	34 53	2		
o′a = $(\bar{1}11):(\bar{1}00)$	—	—	—	70 17	—		
co = $(001):(111)$	3	33 35– 33 58	33 45	33 48	3		
op = $(111):(110)$	3	42 29– 42 35	42 31	42 31	0		
cp = $(001):(110)$	21	76 9– 76 33	76 19	*	—	76 24	
po′ = $(110):(11\bar{1})$	24	58 45– 59 0	58 54	58 53	1	58 41	
o′c = $(11\bar{1}):(00\bar{1})$	21	44 27– 44 59	44 47	44 48	1	44 33	
bn = $(010):(121)$	—	—	—	55 1	—		
no = $(121):(111)$	—	—	—	15 42	—		
bo = $(010):(111)$	—	—	—	70 43	—		
os = $(111):(101)$	—	—	—	19 17	—		
bo′ = $(010):(\bar{1}11)$	32	65 8– 65 20	65 15	65 16	1		
o′s′ = $(\bar{1}11):(\bar{1}01)$	—	—	—	24 44	—		
o′o′ = $(\bar{1}11):(\bar{1}\bar{1}1)$	16	49 21– 49 40	49 30	49 28	2		
sq = $(101):(011)$	—	—	—	37 19	—		
qp = $(011):(\bar{1}10)$	8	87 54– 88 5	88 1	88 4	3		
ps = $(\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 37	—		
pq = $(\bar{1}10):(0\bar{1}\bar{1})$	8	91 55– 92 6	91 59	91 56	3		
s′q = $(\bar{1}01):(011)$	—	—	—	45 6	—		
qn = $(011):(121)$	—	—	—	26 10	—		
np = $(121):(110)$	—	—	—	36 28	—		
qp = $(011):(110)$	10	62 29– 62 39	62 34	62 38	1		
ps′ = $(110):(10\bar{1})$	—	—	—	72 21	—		
pq = $(110):(0\bar{1}\bar{1})$	10	117 21–117 31	117 26	117 27	1		
r′o′ = $(\bar{2}01):(\bar{1}11)$	34	35 11– 35 25	35 18	35 16	2		
o′p = $(\bar{1}11):(110)$	33	91 49– 92 2	91 55	91 57	2		
pr′ = $(110):(20\bar{1})$	33	52 38– 52 54	52 47	52 47	0		
Total number of measurements...	366						

Cleavage.—The crystals cleave fairly readily parallel to $r'\{\bar{2}01\}$, as is general throughout this isomorphous series.

Crystallisation in a Magnetic Field.—As the result of a series of experiments on the deposition of various salts from their saturated solutions under the influence of a magnetic field, St. Meyer* found that in the case of ammonium ferrous sulphate tabular crystals separate, the shorter diagonal of which coincides with the lines of force; this diagonal is parallel to the symmetry plane, and it would appear from St. Meyer's description that the plates are parallel to $r'\{\bar{2}01\}$.

Rapidity of Growth of Different Faces and the Correct Setting.—The exceptional predominance of the orthopinakoid of the second order $r'\{\bar{2}01\}$ formed the subject of the investigation of Wulff† already alluded to. He found the relative rapidity of growth of the various forms to be in the following ascending order: $r'\{\bar{2}01\}$, $p\{110\}$, $c\{001\}$, $o\{111\}$, $o'\{\bar{1}11\}$, and $q\{011\}$. He gives an interesting figure, which is reproduced somewhat smaller in fig. 5, representing the result of immersing a crystal of ammonium zinc

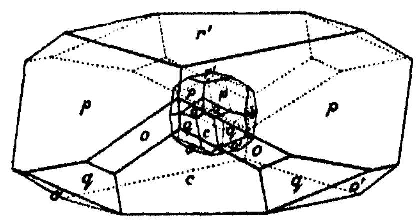


FIG. 5.—A Crystal of Ammonium Ferrous Sulphate growing on one of Ammonium Zinc Sulphate.

sulphate, with precisely equally developed faces, in a slightly supersaturated solution of ammonium ferrous sulphate. The crystal was suspended in the solution by means of a platinum wire hook. According to the experience of both von Hauer and Wulff ammonium ferrous sulphate is the most soluble double sulphate of the series, so that a crystal of ammonium zinc sulphate does not dissolve in a saturated solution of ammonium ferrous sulphate, but, on the contrary, the latter salt at once begins to crystallise as a layer or zonal overgrowth on the crystal of the ammonium zinc salt. Instead, however, of the equal continuation of growth on the equally grown different faces of the latter salt, the resulting crystal at the end of another similar period of time shows the relative development of faces represented in fig. 5, which is drawn from the correct relative amounts of development already described as having been determined by Wulff. First comes $r'\{\bar{2}01\}$ largely

* St. Meyer, 'Sitzungsber. d. Akad. d. Wiss. Wien,' 1899, vol. 108, (IIA), p. 513.

† G. Wulff, 'Zeitschr. für Kryst.,' 1901, vol. 34, p. 486.

predominating, then next in successive order $p\{110\}$ and $c\{001\}$. For the slower the deposition of molecules on any given face, the more does that face predominate, on account of the more rapid growth of the crystal substance on its margins by the more rapid growth of the neighbouring faces.

It is to be remembered in this connection that the following facts have been clearly proved by the work of Bravais, Sohncke, and Curie, and again confirmed more recently by the researches both of Wulff and of von Fedorow.

The faces which are most frequently developed on crystals, and also those which predominate as regards extent of development, as well also as the cleavage planes and those parallel to which tabularity occurs, are precisely those which are most densely strewn with the points of the space-lattice.

With reference to the remarkable predominance of $r'\{\bar{2}01\}$ on ammonium ferrous sulphate, Wulff goes so far as to consider it fundamental, and proposes a new setting of the crystal in which the pair of parallel r'-faces are taken as those of the basal plane $\{001\}$. The next form in importance p becomes $\{1\bar{1}1\}$ on this setting. The crystal is represented in fig. 5 in accordance with it.

It must be remembered, however, that this predominant development of r' is an exceptional one, when the whole isomorphous series is considered. Among the 38 salts of the series which have now been exhaustively dealt with by the author only one, rubidium cadmium sulphate, has shown a similar predominance of r', although in four other cases this form has been observed largely but not predominatingly developed, namely, in rubidium ferrous sulphate, cæsium ferrous sulphate, potassium copper sulphate, and cæsium copper sulphate. In general throughout the series the faces of the primary prism $p\{110\}$ and of the basal plane $c\{001\}$ vastly predominate, with the faces of $q\{011\}$ and $o'\{\bar{1}11\}$ following closely after in relative extent of development. Wulff himself mentions that $p\{110\}$ predominates on the crystals of ammonium zinc sulphate, even to as large an extent as does $r'\{\bar{2}01\}$ on ammonium ferrous sulphate. He ascribes the difference as due to the mode of growth of the two salts in the crystallisation vessel. Those of the ammonium zinc salt usually grow with either $p\{110\}$ or $c\{001\}$ in contact with the bottom of the vessel, and very rarely on $b\{010\}$, a form which is singularly seldom well developed, as regards extent, throughout the whole series. Moreover, the ammonium zinc salt never grows upon an $r'\{\bar{2}01\}$ face. On the other hand, ammonium ferrous sulphate crystals grow best of all on the r'-plane, as well as readily upon $c\{001\}$ and $p\{110\}$, but never upon $b\{010\}$. It would thus appear that Wulff is correct as regards this explanation of the difference of habit.

It is interesting to remark that this fact of ready growth on the r'-plane may be connected with St. Meyer's observation, that when ammonium ferrous sulphate is crystallised in a magnetic field the crystals take the form of plates parallel to $r'\{\bar{2}01\}$. For, as this salt is highly magnetic, there can be no surprise if the earth's magnetism should produce the same effect as an artificial magnetic field, and cause the deposition of tabular crystals parallel to $r'\{\bar{2}01\}$.

Moreover, as regards habit, it has been shown by the author that the alkali base present, in the cases of potassium, rubidium, and cæsium, has a definite influence on the habit, which is most marked in the case of the basal plane $c\{001\}$; the faces of this form are, as a rule, relatively very large in the potassium salt, very narrow in the cæsium salt, and of intermediate size in the rubidium salt. This influence is absent in the non-metallic ammonium salt, leaving other influences more free to act.

The "setting" of the crystals of the salts of this series has been gone carefully into by von Fedorow.* The setting employed by the author,† in this and all previous communications concerning this series, is that which was given by Murmann and Rotter, and, as it is the most natural one in precise keeping with the undoubtedly holohedral monoclinic symmetry of the crystals, was adopted by the author in the absence of any opposing reason.

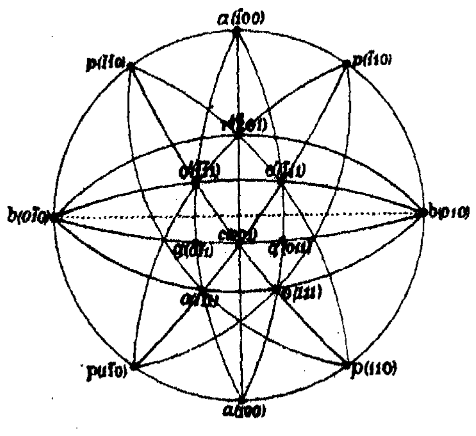
It has been shown that this setting is preferable to that proposed by Wulff, when the development of faces throughout the whole series is generally considered, and von Fedorow confirms this view from the standpoint of the rule regarding reticular density. Both the settings of Wulff and of the author agree with monoclinic symmetry, but Wulff rotates the crystal about the symmetry axis until r' becomes the basal plane instead of c, both these planes being in the orthozone at right angles to the symmetry plane.

Von Fedorow, however, proposes yet another setting, which he finds to agree better with the rule of reticular density. But it is, in the opinion of the author, much to its disadvantage that the reason for it is really based on the peculiar form of the geometrical theory of crystal structure which has been advanced by von Fedorow, and particularly on that part of it which is not so firmly grounded as that which refers only to the derivation of the 230 possible point-systems concerned in crystal structure; this more hypothetical part refers to the nature of what the points represent, and to von Fedorow's idea that all crystals are of either cubic or hexagonal type or of one of those types more or less deformed, which he terms pseudo-cubic

* E. von Fedorow, 'Zeitschr. für Kryst.,' 1909, vol. 46, p. 258.

† 'Journ. Chem. Soc.,' 1893, vol. 63, p. 337; see fig. 1, p. 343, for stereographic projection.

and pseudo-hexagonal or hexagonaloid. Here, like Pope and Barlow in their valency theory, von Fedorow leaves solid incontrovertible ground, which has been fully substantiated quite recently by the interesting experiments of Laue, Friedrich, and Knipping* in obtaining photographic reflections of X-rays from the planes of atoms within the crystal, the planes involved being those containing the points (representing similar and similarly situated atoms) of the underlying space-lattice, as the photographs always show spots arranged with holohedral and never hemihedral symmetry. Von Fedorow retains the same vertical axis as the author in his proposed setting, but rotates the crystal for 180° around it. If, instead of arranging the stereographic projection of a monoclinic crystal as usual in this country, projected on the symmetry plane, we retain the method adopted for the other crystal systems, of making the primitive circle of the projection the prism and primary pinakoid zone, with the poles (100) and ($\bar{1}$00) in front and behind and (010) and (0$\bar{1}$0) right and left respectively, a method which is often adopted in Germany for monoclinic crystals, we have the projection given in fig. 6. The setting of von Fedorow is represented in fig. 7, which is evidently the same as fig. 6 rotated for 180° in the plane of the paper, that is, about the vertical axis represented in plan by the centre of the projection, which in a rhombic crystal would be the position of the facial pole of the basal plane, *c*(001), which pole, however, is now displaced forwards in fig. 6 by the angle of monoclinic tilt 16° 50',



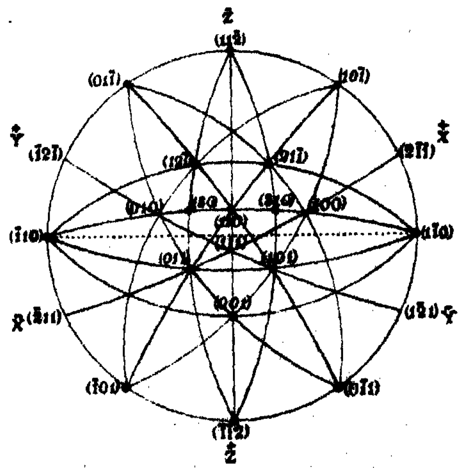


FIG. 6.—Tutton's Setting. FIG. 7.—Von Fedorow's Setting.

Alternative Settings for Double Sulphates with $6H_2O$.

* 'Sitzungsber. (Math.-Phys. Classe) d. K. B. Akad. d. Wiss. München,' 1912, pp. 303 and 363.

and in fig. 7 to the same extent backwards. In both figures the plane of symmetry is represented by the diameter parallel to the longer edges of the page.

While thus von Fedorow merely alters the author's setting by this rotation for 180°, bringing what was the back of the crystal to the front and *vice versâ*, he regards the various poles from an altogether different standpoint. He ignores the monoclinic symmetry, except as being a deformation in one direction, and states that the crystal complex appears to be a hexagonaloid one of cubic type, that is, one of trigonaloid character, which he expresses, in accordance with a method of concise symbols which he employs, thus:—

$$\begin{array}{c} 3o\,;\ +13 \\ 47\tfrac{1}{2} \\ -5\tfrac{1}{2} \end{array}$$

The letter *o* in the top line indicates the octahedral main structure; the 3 in front of it represents the trigonaloid character, which is similar to the rhombohedral one of calcite, but considerably deformed (in one direction) from the form of the regular rhombohedron; the $+13$ signifies the number of degrees of monoclinic deformation, on the $+$ side of the trigonal axis Z, that is, the angle between the centre of the projection, which in a truly trigonal crystal like calcite is occupied by the pole (111), and the actual position of the pole of the possible face which is analogous to (111) on the deformed crystal. The central number $47\frac{1}{2}$ represents the number of degrees in the principal angle (111) : (001), that is, between the basal plane and one of the faces of the primary rhombohedron, on the supposition of trigonaloid character and after imaginary re-deformation of (111) back to true trigonal symmetry, that is, to the centre. The lower number $-5\frac{1}{2}$ represents the angular deviation from 30° of the poles on the primitive circle, that is, of the poles which in trigonal symmetry would correspond to $(\bar{1}01)$ and $(\bar{1}\bar{1}2)$; these are adjacent faces of the two varieties of hexagonal prism in a truly trigonal crystal, and are in the latter 30° apart, but in the neighbourhood of $35\frac{1}{4}$° (the angle *ap*) in this series of double sulphates (35° 13′ in ammonium ferrous sulphate).

Von Fedorow gives the following transformation equations (*loc. cit.*, p. 259) for the conversion of the indices p_1, p_2, p_3, of any face according to the monoclinic setting of the author, to the corresponding indices q_1, q_2, q_3, according to von Fedorow's trigonaloid setting:

$$q_1 : q_2 : q_3 = p_1 - p_2 + 2p_3 : p_1 + p_2 + 2p_3 : -2p_1,$$

or the determinants:

$$\begin{vmatrix} 1 & \bar{1} & 2 \\ 1 & 1 & 2 \\ \bar{2} & \cdot & \cdot \end{vmatrix}$$

The indices of the principal faces according to the two settings are given below, those of the author's setting being in brackets as usual, and those of von Fedorow not, in order to distinguish them:

$$c(001) = 110,\ r'(201) = 001,\ a(100) = 11\bar{2},\ b(010) = \bar{1}10,$$
$$q(011) = 130,\ o'(\bar{1}11) = 011,\ p(110) = 01\bar{1}.$$

It will be clear that the r'-face of the author's setting becomes the rhombohedron face (001) [the $r(001)$ of calcite], and the c-face becomes the face (110) [the $e(110)$ of calcite]. The setting of von Fedorow, thus regarded as a monoclinically deformed rhombohedral one, corresponds to a similarly deformed rhombohedral space-lattice, while the setting of the author corresponds to the second (pinakoidal) monoclinic space-lattice.

The author regards this deformation idea, in cases like this where the difference from 30° is as much as 5½° and the displacement of (111) from the centre no less than 13°, as an unnecessary complication, and one which is not likely to be followed in actual practice by chemists or crystallographers desirous of making use of the great advantages of crystallo-chemical analysis. Moreover, it will be obvious that if we follow von Fedorow all the way, and accept the assumption of a deformed trigonal symmetry, the following important forms or faces are missing, indicated on fig. 7 by their indices, but without pole-dots: {111} the basal plane; four of the six faces of the hexagonal prism of the first order $\{2\bar{1}\bar{1}\}$, for only two, $(11\bar{2})$ and $(\bar{1}\bar{1}2)$, are generally developed, which are the a-faces (100) and $(\bar{1}00)$ of the author's monoclinic setting, the other four faces, $(2\bar{1}\bar{1})$, $(1\bar{2}1)$, $(\bar{2}11)$, and $(\bar{1}2\bar{1})$, having only been seen developed to a measurable extent on one or two crystals of six of the 38 investigated salts of the series as the minute faces p''' (namely, on KCu-, RbCu-, CsCu-, RbCd-, CsCd-, and AmMg-sulphates); and two of the three faces of the primary rhombohedron itself {100}, for only one, (001), is present, while (010) and (100) are generally entirely absent, and have only been seen by the author as minute faces (the m-faces) on three of the 38 salts of the series investigated, namely, KNi-, RbCu-, and CsCd-sulphates. Further, which is even more significant, while it is true that all six faces of the hexagonal prism of the second order $\{10\bar{1}\}$ are developed, four of them are the largely and generally predominatingly developed faces of the primary prism $p\{110\}$ of the author's monoclinic setting, while the other two are very small and frequently absent faces of the clinopinakoid $b\{010\}$; that is, two clearly different and very unequally developed forms make up the six faces which von Fedorow proposes to consider as a hexagonaloid prism. Again, the cleavage is only developed parallel to one plane, that of the pair of parallel faces of $r'\{\bar{2}01\}$, that is,

only parallel to one of the three planes of the pseudo-rhombohedron of von Fedorow.

Thus, while it may be true that the faces of the pseudo-rhombohedron possess the maximum reticular density, still there appear to be so many deficiencies as regards development of primary planes, either as faces or cleavage planes, that the author much prefers to accept the simple and obvious monoclinic symmetry of both faces and cleavage as determinative of the setting; and as Wulff's setting is still less to be preferred, both for the reasons given by the author and for the additional ones also advanced by von Fedorow, it is considered preferable to retain the setting which has been adopted throughout all these investigations.

If a clearly hexagonal habit were presented, and all the essential faces well developed, such as in the cases of the simple rhombic sulphates and selenates of the alkalies, where the differences from exactly 30° are only a few minutes, the presence of a pseudo-hexagonal space-lattice could with reason be accepted, and in the descriptions of those salts the author has given the dimensions of the elementary cells of the space-lattice on such an assumption. But in this monoclinic series of double salts such is not the case.

Etch-Figures.—The investigation by Baumhauer* of the etch-figures produced by a small quantity of water on the principal faces afforded results conclusively indicating the presence of holohedral monoclinic symmetry. Besides ammonium ferrous sulphate two other salts of the series were studied, namely, potassium and ammonium nickel sulphates. Two illustrations are reproduced from Baumhauer's memoir, in figs. 8 and 9, but with his lettering of the faces replaced by the letters now assigned to those faces.

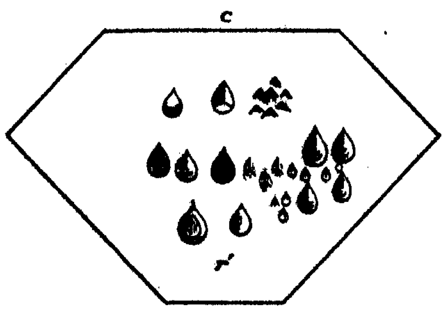


FIG. 8.—Etch-figures on Ammonium Ferrous Sulphate.

Fig. 8 shows the character of the etch-figures on the predominating faces of r'{201} in the case of ammonium ferrous sulphate. Fig. 9 reproduces those

* H. Baumhauer, 'Pogg. Ann. d. Phys.,' 1873, vol. 150, p. 619.

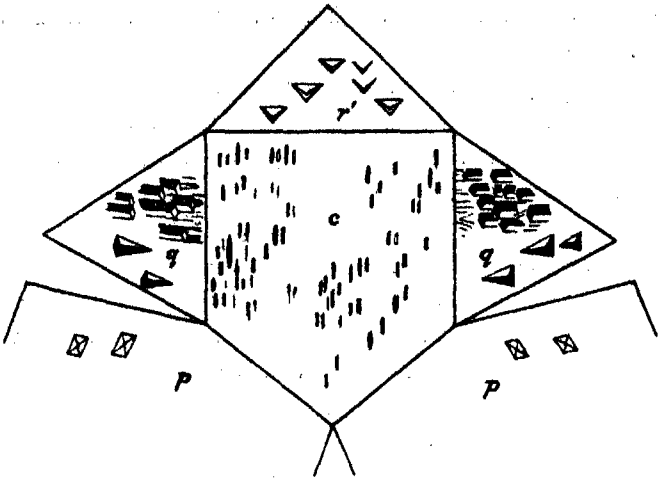


FIG. 9.—Etch-figures on Potassium Nickel Sulphate.

on the four principal forms $c\{001\}$, $p\{110\}$, $q\{011\}$, and $r'\{\bar{2}01\}$ of potassium nickel sulphate. Those on ammonium nickel sulphate were also very similar.

It will be clear that these etch-figures in every case are symmetrical to the single plane of symmetry $b\{010\}$, which is at right angles to the plane of the paper and parallel to the longer sides of the page; they also accord with the presence of a digonal axis of symmetry perpendicular to the plane of symmetry (parallel to the shorter edges of the page). They possess, consequently, both the elements of monoclinic symmetry, and therefore the crystals are holohedral. Moreover, the etch-figures are quite different from such as are usually afforded by a crystal of trigonal symmetry.

Comparison of the Morphological Constants of the Four Salts of the Iron Group.—The crystal-angles, axial angles, and axial ratios of the potassium, rubidium, cæsium, and ammonium ferrous sulphates are compared in the next two tables.

As regards the monoclinic axial angle β, its value for the ammonium salt is almost identical with that for the cæsium salt. It is noteworthy that a like fact has been observed in all the other groups yet studied, the sulphate and selenate groups containing zinc and magnesium respectively, and the magnesium group of double chromates.

With reference to the axial ratios, it is only possible to infer that the values for the ammonium salt are so similar to those for the analogous alkali-metal salts that true isomorphism undoubtedly exists. It is somewhat singular that the a-values are identical for three of the salts, potassium, rubidium, and ammonium ferrous sulphates.

Comparison of the Interfacial Angles.

Angle.	KFe sulphate.	RbFe sulphate.	CsFe sulphate.	AmFe sulphate.
	° ′	° ′	° ′	° ′
$ac = (100):(001)$	75 28	74 16	73 8	73 10
$as = (100):(101)$	46 9	45 24	44 34	44 52
$sc = (101):(001)$	29 19	28 52	28 34	28 18
$cr' = (001):(\bar{2}01)$	63 21	64 8	65 8	64 36
$cs' = (001):(\bar{1}01)$	38 23	38 38	39 7	38 36
$s'r' = (\bar{1}01):(\bar{2}01)$	24 58	25 30	26 1	26 0
$r'a = (\bar{2}01):(\bar{1}00)$	41 11	41 36	41 44	42 14
$ap = (100):(110)$	35 36	35 23	34 40	35 13
$pp' = (110):(120)$	19 28	19 28	19 28	19 28
$p'b = (120):(010)$	34 56	35 9	35 43	35 19
$pb = (110):(010)$	54 24	54 37	55 11	54 47
$cq = (001):(011)$	25 56	25 43	25 21	25 24
$qb = (011):(010)$	64 4	64 17	64 39	64 36
$ao = (100):(111)$	49 21	48 35	47 42	48 1
$oq = (111):(011)$	27 37	27 17	27 6	26 49
$aq = (100):(011)$	76 58	75 52	74 48	74 50
$qo' = (011):(\bar{1}11)$	34 35	34 51	35 20	34 53
$o'a = (\bar{1}11):(\bar{1}00)$	68 27	69 17	69 52	70 17
$co = (001):(111)$	34 56	34 26	33 57	33 48
$op = (111):(110)$	43 17	42 48	42 16	42 31
$cp = (001):(110)$	78 13	77 14	76 13	76 19
$po' = (110):(11\bar{1})$	57 18	57 57	58 38	58 58
$o'c = (11\bar{1}):(00\bar{1})$	44 34	44 49	45 9	44 43
$bo = (010):(111)$	70 6	70 23	70 50	70 43
$os = (111):(101)$	19 54	19 37	19 10	19 17
$bo' = (010):(\bar{1}11)$	65 20	65 15	65 22	65 16
$o's' = (\bar{1}11):(\bar{1}01)$	24 40	24 45	24 38	24 44
$sq = (101):(011)$	38 22	37 55	37 28	37 19
$qp = (011):(\bar{1}10)$	85 55	87 1	88 20	88 4
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 43	55 4	54 12	54 37
$s'q = (\bar{1}01):(011)$	45 10	45 16	45 29	45 6
$qp = (011):(110)$	64 1	63 14	62 38	62 33
$ps' = (110):(10\bar{1})$	70 49	71 30	71 53	72 21
$r'o' = (\bar{2}01):(\bar{1}11)$	34 32	34 57	35 13	35 16
$o'p = (\bar{1}11):(110)$	93 12	92 37	92 34	91 57
$pr' = (110):(20\bar{1})$	52 16	52 26	52 13	52 47

From the table of crystal angles and a critical analysis of it are to be derived the following facts: In the cases of 32 of the 36 angles compared the angular change introduced by the replacement of potassium by ammonium occurs in the same direction (increase or decrease of angle) as when rubidium or cæsium is the replacing element, and the few exceptions (the angles bo', $o's'$, $s'q$, and pr') occur in cases where the change is very minute. The effect of the replacement of potassium by ammonium is thus to call forth in general an alteration in the crystal angles of the same sign as when rubidium

or cæsium is the replacing base, in which latter cases the changes have been previously shown to follow the order of the atomic weights of the alkali metals.

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	a : b : c
Potassium ferrous sulphate	104° 32′	0·7377 : 1 : 0·5020
Rubidium ,, ,,	105 44	0·7377 : 1 : 0·5004
Ammonium ,, ,,	106 50	0·7377 : 1 : 0·4960
Cæsium ,, ,,	106 52	0·7261 : 1 : 0·4953

In 29 of these 32 cases the amount of the angular change is larger than when rubidium replaces potassium, and in the greater number (24) it is either approximately the same (13 cases) as when cæsium is introduced or greater (11 cases) than that amount. The average and maximum changes of angle for the various replacements are set out in the next table:—

Replacement.	Average change.	Maximum change.
K by Rb	32′	72′ = 1° 12′
K by Cs	65′ = 1° 5′	145′ = 2° 25′
K by NH_4	62′ = 1° 2′	148′ = 2° 28′

It is thus clear that both the average and the maximum changes of angle which occur when potassium is replaced by ammonium are almost exactly identical with those evoked by the introduction of cæsium instead of potassium, and twice as great as when rubidium is the replacing element. Identical conclusions were also drawn from the investigation of the magnesium and zinc groups of double sulphates and selenates. They accord completely with the eutropic character of the relationships between the three alkali-metal salts, and with the merely isomorphous and not eutropic nature of the occurrence of the ammonium salt in the group. As regards the average and maximum changes of crystal angle, the three eutropic salts show direct proportionality to the atomic weights of the three metals.

Volume.

Relative Density.—Seven determinations of specific gravity were made with small perfect crystals selected from five different crops, by the Retgers immersion method, using a mixture of methylene iodide and benzene as the immersion liquid. The following results for the heaviest crystal in each case were obtained:—

I.	Density for 16°·7/4°	1·8618	For 20°/4°	1·8612
II.	„ 17°·8/4°	1·8616	„	1·8612
III.	„ 17°·6/4°	1·8621	„	1·8616
IV.	„ 18°·1/4°	1·8631	„	1·8627
V.	„ 15°·8/4°	1·8647	„	1·8639
VI.	„ 18°·5/4°	1·8638	„	1·8635
VII.	„ 17°·4/4°	1·8649	„	1·8644

The value accepted for 20°/4° is thus **1·864.**

Earlier values (none of them recent) by various workers have varied as much as from 1·81 to 1·89. Considering the excellent unanimity of the above results this wide difference is difficult to understand.

Molecular Volume.—$\frac{M}{d} = \frac{389{\cdot}32}{1{\cdot}864} = 208{\cdot}86.$

Molecular Distance Ratios (*topic axial ratios*).—

$$\chi : \psi : \omega = 6{\cdot}2094 : 8{\cdot}4172 : 4{\cdot}1749.$$

Redeterminations of the Densities of Potassium, Rubidium, and Cæsium Ferrous Sulphates.—In order to render valid all comparisons between the volume constants of these four salts of the ferrous iron group, a series of redeterminations of the specific gravities by the Retgers immersion method have been carried out for the three alkali-metal salts; for the earlier determinations recorded in the author's 1896 memoir* were carried out by the pyknometer method, which is liable to afford lower values for the density, owing to the result being an average one for a large number of crystals in the finely powdered condition, whereas the Retgers method affords the density of the heaviest and therefore most cavity-free crystal.

The results are given below :—

Potassium Ferrous Sulphate, $K_2Fe(SO_4)_2.6H_2O$.

I.	Density for 15°·8/4°	2·1797	For 20°/4°	2·1788
II.	„ 15°·8/4°	2·1785	„	2·1776
III.	„ 16°·7/4°	2·1748	„	2·1741
IV.	„ 16°·8/4°	2·1758	„	2·1751

In determination I the heaviest crystal showed a tendency to rise in the immersion liquid, and in determination III to sink. In determinations II and IV the heaviest crystal remained in the middle of the liquid. The accepted value is therefore **2·177**, for 20°/4°.

Rubidium Ferrous Sulphate, $Rb_2Fe(SO_4)_2.6H_2O$.

I.	Density for 17°·0/4°	2·5184	For 20°/4°	2·5177
II.	„ 19°·1/4°	2·5181	„	2·5179

The accepted value is thus **2·518** for 20°/4°.

* 'Journ. Chem. Soc.,' 1896, vol. 69, p. 344.

Cæsium Ferrous Sulphate, $Cs_2Fe(SO_4)_2.6H_2O$.

I. Density for 18°·5/4°	...... 2·7964	For 20°/4°	......	2·7960
II. „ 18°·4/4°	...... 2·7959	„	......	2·7955

The value accepted for 20°/4° is consequently **2·796.**

The values obtained by the pyknometer method in the year 1896 were respectively 2·169, 2·516, and 2·791 for these potassium, rubidium, and cæsium salts containing iron. The new results are thus in all three cases somewhat higher, which was to be expected for the most perfectly cavity-free crystals, perfect little crystals quite free from turbidity having been in all cases used in these new determinations. The highest individual results in 1896 were 2·172, 2·520, and 2·793 for the three respective salts.

Comparison of the Volume Constants of the Iron Group.—The densities and topic axial ratios of the four salts are compared in the next table:—

Volume Constants of the Iron Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				$\chi : \psi : \omega$
KFe sulphate	431·16	2·177	198·05	6·0583 : 8·2056 : 4·1192
RbFe „	523·26	2·516	207·81	6·1692 : 8·3628 : 4·1848
NH_4Fe „	389·32	1·864	208·86	6·2094 : 8·4172 : 4·1749
CsFe „	617·26	2·796	220·77	6·2621 : 8·6242 : 4·2716

It will be clear from this table that the molecular volume and topic axial ratios of the ammonium salt are very close to those of the rubidium salt, a result in keeping with the facts derived from the zinc and magnesium sulphate, selenate, and chromate groups previously investigated. As regards the molecular volume, the value for ammonium ferrous sulphate is about one unit higher than that for the rubidium salt, and in the cases of the topic axial ratios the values for χ and ψ are slightly higher and for ω very slightly lower. These small differences between the volume constants of the ammonium and rubidium salts are very much smaller than the differences between the values for the three alkali-metal salts; between the potassium and cæsium salts there is a difference of molecular volume of no less than 22·72 units, and between the potassium and rubidium salts of 9·76 units.

It is thus clear that the replacement of potassium by ammonium is accompanied by practically the same amount of extension of the crystal structure as when rubidium is introduced for potassium, and by a very much smaller change of volume than when cæsium is introduced instead of potassium. Obviously also, there is scarcely any change at all of volume or

alteration of the molecular distances or of the dimensions of the space-lattice unit cell, when rubidium and ammonium are interchanged for one another. This important result is in line with what was discovered by the investigation of the zinc and magnesium sulphate and selenate groups, and of the magnesium chromate group.

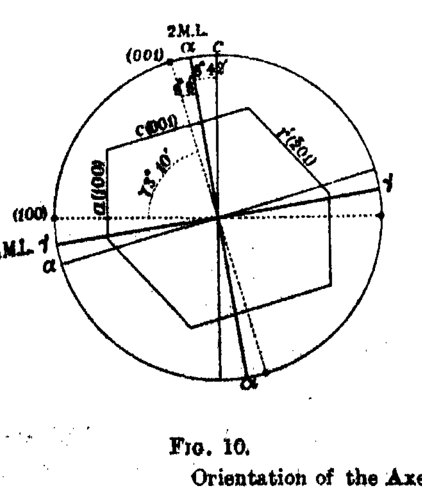
Optics.

Orientation of the Optical Indicatrix.—The plane of the optic axes is the symmetry plane $b\{010\}$, as is the case throughout the whole series. The first median line corresponds to the γ refractive index, and the second median line to the α index, the double refraction being of positive sign. The symmetry axis b is the direction corresponding to the β index.

Determinations of extinction in the symmetry plane were carried out with the aid of two excellent section-plates, ground parallel to the symmetry plane with the aid of the cutting and grinding goniometer. The following were the results, which express the position of the second median line behind the normal to $c\{001\}$, for sodium light.

	°	′
Plate I	8	10
,, II	8	6
Mean value	8	8

Hence, the first median line is inclined 8° 8′ to the inclined axis a, and, as the axial angle ac = 73° 10′, the same median line is inclined 8° 42′ to the normal to $a\{100\}$, and 98° 42′ to the vertical axis c, forwards, for sodium light. The second median line is 8° 8′ behind the normal to $c\{001\}$, and lies 8° 42′ forwards from the vertical axis c. This orientation will be clear from fig. 10. According to Murmann and Rotter the first median line is inclined



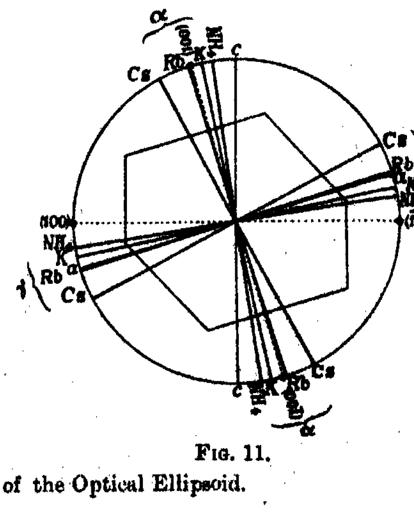


FIG. 10. FIG. 11.

Orientation of the Axes of the Optical Ellipsoid.

99° 43′ to the *c*-axis, and 7° 5′ to the *a*-axis. According to Miller the former angle is 99° 6′.

Comparison of the Positions of the Optical Ellipsoids of the Iron Group.—The optical ellipsoid rotates about the symmetry axis *b* when one alkali base is replaced by another, and the order, in front of the vertical axis, is: Ammonium salt, potassium salt, rubidium salt, cæsium salt, as will be clear from fig. 11 and the following table. The latter shows the positions, for the four salts of the group, of that axis of the ellipsoid which is the second median line and corresponds to the refractive index α.

Inclination of the α-Axis of the Indicatrix to the Vertical Axis *c*, in front, for Na Light.

		°	′
NH_4Fe sulphate	....	8	42
KFe „	....	11	57
RbFe „	....	17	9
CsFe „	....	28	17

The dispersion of the median lines in the symmetry plane is very small for all four salts, not exceeding 10 minutes between red Li and greenish-blue F light; so that the positions stated above are valid for any wave-length within the limits of experiment. The position of the ellipsoid for the ammonium salt is so that the α-axis lies nearest the vertical axis *c* of the crystal, 8° 42′ in front of it; while the ellipsoid rotates so that the α-axis moves further and further away from the vertical axis as potassium, rubidium, and cæsium successively replace the ammonium, the rotation being a function of the atomic weight of the alkali metals in the cases of these three metallic salts. These rules are exactly similar to those found for the magnesium and zinc groups, both double sulphates and double selenates.

Refractive Indices.—Six excellent 60°-prisms were ground by means of the cutting and grinding goniometer, from perfectly clear and transparent crystals, selected from three different crops. Each prism afforded two indices directly, three of them gave α and β, two yielded α and γ, and the sixth prism furnished β and γ. The results are compiled in the next table.

According to Murmann and Rotter the β-indices for red, yellow, and green light are respectively 1·487, 1·490, and 1·492.

The intermediate index β, corrected to a vacuum (correction $+0·0004$), is expressed for any wave-length λ by the following general formula:

$$\beta = 1·4784 + \frac{494\ 204}{\lambda^2} - \frac{885\ 610\ 000\ 000}{\lambda^4} + \ldots.$$

The α-indices are also reproduced by the formula if the constant 1·4784 is reduced by 0·0046, and the γ-indices if it is increased by 0·0074.

Refractive Indices of Ammonium Ferrous Sulphate.

Index.	Nature of light.	Prisms 1, 2, 3.	Prisms 4, 5.	Prism 6.	Mean index.
α. Vibration direction parallel to second median line.	Li	1·4836–44	1·4837–9		1·4839
	C	1·4841–7	1·4843–4		1·4844
	Na	1·4866–74	1·4867–8		1·4870
	Tl	1·4898–900	1·4893–6		1·4896
	Cd	1·4906–15	1·4909–10		1·4911
	F	1·4922–30	1·4925–6		1·4926
	G	1·4969–74	1·4970–1		1·4971
β. Vibration direction parallel to symmetry axis *b*.	Li	1·4881–9		1·4881	1·4885
	C	1·4886–93		1·4886	1·4890
	Na	1·4910–20		1·4912	1·4915
	Tl	1·4940–5		1·4939	1·4942
	Cd	1·4954–62		1·4954	1·4957
	F	1·4969–79		1·4970	1·4972
	G	1·5016–24		1·5020	1·5019
γ. Vibration direction parallel to first median line.	Li		1·4954–60	1·4956	1·4957
	C		1·4959–65	1·4961	1·4962
	Na		1·4989–91	1·4987	1·4989
	Tl		1·5018–8	1·5016	1·5017
	Cd		1·5032–2	1·5032	1·5032
	F		1·5046–9	1·5046	1·5047
	G		1·5094–4	1·5093	1·5094

Mean of α, β, and γ for Na light = 1·4925.

Change of Refraction by Rise of Temperature.—Determinations of refractive index at 60° C. were carried out with two of the prisms, which furnished α and β, and α and γ, respectively. The results are combined in the following table; the two series of α-values were practically identical, the greatest deviation for any one wave-length being only 0·0002, so that the table is a very trustworthy one.

Refractive Indices of AmFe Sulphate at 60° C.

	α.	β.	γ.
Li	1·4825	1·4865	1·4939
C	1·4830	1·4870	1·4944
Na	1·4857	1·4898	1·4971
Tl	1·4882	1·4925	1·4998
Cd	1·4898	1·4941	1·5014
F	1·4915	1·4958	1·5031

These values are lower than those for the ordinary temperature, the α-values being on the average 0·0013 lower, the β-values 0·0017 smaller, and the γ-values 0·0018 less.

Comparison of the Refractive Indices of the Four Salts of the Iron Group.—The indices of ammonium, potassium, rubidium, and cæsium ferrous sulphates are compared in the next table.

From this table it will be apparent that the whole of the refractive indices, and also the mean refractive index, of the ammonium salt are close to the analogous values for the rubidium salt and just slightly higher, but not nearly so high as those of the cæsium salt. Thus the indices of the ammonium salt lie between those of the rubidium and cæsium salts, and quite near to those of the rubidium salt. In all the other groups investigated, the zinc and magnesium sulphate and selenate groups and the magnesium chromate group, the indices of the ammonium salt also lie between those of the rubidium and cæsium salts, sometimes nearer the former and sometimes nearer the latter.

The Double Refraction, as afforded by the difference between the two extreme indices α and γ for sodium light, in the case of the ammonium salt, also lies between the values for the rubidium and cæsium salts, but as regards this property nearer to the cæsium salt.

Comparison of the Refractive Indices.

Index.	Light.	KFe sulphate.	RbFe sulphate.	NH_4Fe sulphate.	CsFe sulphate.
α	Li	1·4731	1·4789	1·4839	1·4976
	C	1·4735	1·4793	1·4844	1·4980
	Na	1·4759	1·4815	1·4870	1·5008
	Tl	1·4782	1·4839	1·4896	1·5028
	F	1·4811	1·4870	1·4926	1·5061
	G	1·4852	1·4916	1·4971	1·5105
β	Li	1·4795	1·4847	1·4885	1·5007
	C	1·4799	1·4851	1·4890	1·5011
	Na	1·4821	1·4874	1·4915	1·5035
	Tl	1·4847	1·4898	1·4942	1·5061
	F	1·4877	1·4929	1·4972	1·5093
	G	1·4920	1·4978	1·5019	1·5137
γ	Li	1·4941	1·4949	1·4957	1·5065
	C	1·4945	1·4953	1·4962	1·5069
	Na	1·4969	1·4977	1·4989	1·5094
	Tl	1·4995	1·5003	1·5017	1·5121
	F	1·5028	1·5034	1·5047	1·5153
	G	1·5071	1·5080	1·5094	1·5198
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4850	1·4889	1·4925	1·5044
Double refraction, $Na_{\gamma-\alpha}$		0·0210	0·0162	0·0119	0·0091

Comparison of the Axial Ratios of the Optical Ellipsoid.—The values of the ratios of the axes of the optical indicatrix and of the optical velocity ellipsoid of ammonium ferrous sulphate have been calculated, and are compared with those for the alkali-metal salts in the following table. The comparison is made both when the β-axis of each salt is taken = 1, and also when the

β-axis of the potassium salt is taken as unity, in order in the latter case to ascertain the effect of replacing one alkali base by another on the dimensions of the two ellipsoids.

Axial Ratios of the Optical Indicatrix.

	$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KFe sulphate......	0·9958 : 1 : 1·0100	0·9958 : 1 : 1·0100
RbFe ,, ...	0·9960 : 1 : 1·0069	0·9996 : 1·0036 : 1·0105
NH_4Fe ,, ...	0·9970 : 1 : 1·0050	1·0033 : 1·0063 : 1·0113
CsFe ,, ...	0·9979 : 1 : 1·0039	1·0123 : 1·0144 : 1·0184

Axial Ratios of the Optical Velocity Ellipsoid.

	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$
KFe sulphate......	1·0042 : 1 : 0·9901	1·0042 : 1 : 0·9901
RbFe ,, ...	1·0040 : 1 : 0·9931	1·0004 : 0·9964 : 0·9896
NH_4Fe ,, ...	1·0030 : 1 : 0·9951	0·9967 : 0·9937 : 0·9888
CsFe ,, ...	1·0021 : 1 : 0·9961	0·9879 : 0·9858 : 0·9819

These numbers unite in indicating that the dimensions of the optical ellipsoid, whether it be the indicatrix or the velocity ellipsoid, in the case of the ammonium salt of the iron group lie between those of the rubidium and cæsium salts, and when the total change of dimensions is considered, as given by the right-hand set of ratios for each ellipsoid, the values lie much closer to those of the rubidium salt than to those of the cæsium salt. It must be remembered, however, that the ellipsoid rotates about the symmetry axis on each replacement, in the order given in the table on p. 378 and illustrated in fig. 11.

Molecular Optical Constants.—These constants have been calculated for the ammonium salt, from the specific gravity and the refractive indices, and the values are compared in the next three tables with the corresponding values for the three alkali-metal salts of the iron group. These latter values have been recalculated, employing the new values for the specific gravities given in this memoir, the results of the redeterminations by the immersion method.

Table of Specific Refraction and Dispersion (Lorenz).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$. For ray C(H$\alpha$).			For ray Hγ near G.			Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmFe ...	0·1536	0·1548	0·1568	0·1570	0·1583	0·1603	0·0034	0·0035	0·0035
KFe	0·1290	0·1305	0·1338	0·1317	0·1333	0·1367	0·0027	0·0028	0·0029
RbFe......	0·1127	0·1139	0·1159	0·1151	0·1163	0·1184	0·0024	0·0024	0·0025
CsFe	0·1048	0·1053	0·1064	0·1071	0·1076	0·1087	0·0023	0·0023	0·0023

Table of Molecular Refraction and Dispersion (Lorenz).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.						Molecular dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C(Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KFe	55·61	56·25	57·71	56·78	57·46	58·95	1·17	1·21	1·24
RbFe	58·96	59·57	60·63	60·24	60·84	61·95	1·28	1·27	1·32
AmFe	59·80	60·28	61·08	61·13	61·63	62·40	1·33	1·35	1·37
CsFe	64·71	65·05	65·69	66·08	66·43	67·09	1·37	1·38	1·40

Molecular Refraction (Gladstone and Dale).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KFe sulphate	93·78	95·05	97·94	95·59
RbFe "	99·60	100·81	102·93	101·11
AmFe "	101·17	102·13	103·64	102·31
CsFe "	109·94	110·62	111·91	110·82

From these tables the following facts are to be derived:—

The specific refraction and dispersion of the ammonium salt are considerably higher than those of the alkali-metal salts of the group, which three latter salts exhibit values progressively diminishing with the atomic weight of the alkali metal.

The molecular dispersion of the ammonium salt lies between the values for the rubidium and cæsium salts, and nearer to those of the cæsium salt.

The molecular refraction of the ammonium salt, whether calculated by means of the formula of Lorenz or by that of Gladstone and Dale, is very close to, and very slightly higher than, the corresponding (as regards direction in the crystal and the optical ellipsoid) value for the rubidium salt. The mean molecular refraction, in which the influence of direction in the crystal is eliminated, follows precisely the same rule. The rule is, indeed, common to all the double sulphate, selenate and chromate groups of this series yet investigated.

Optic Axial Angle.—Three excellent pairs of section-plates perpendicular to the first and second median lines were obtained by grinding, with the aid of the cutting and grinding goniometer, each pair from crystals belonging

to a separate crop. They all furnished magnificent interference figures when immersed in monobromonaphthalene, with very small inner rings and very sharp hyperbolic brushes, and thus afforded excellent determinations of $2H_a$ with plates 1, 2, and 3, perpendicular to the first median line, and of $2H_o$ with the plates $1a$, $2a$, and $3a$, perpendicular to the second median line. Plates 1 and 2 also gave good interference figures in air, and consequently enabled excellent determinations of 2E to be made; but plate 3 was too thick to enable the hyperbolæ to be brought quite up to the double spider lines for measurement of 2E.

The results are given in the next two tables.

Apparent Optic Axial Angle in Air, 2E, of AmFe Sulphate.

Light.	Plate 1.	Plate 2.	Mean 2E.
	° ′	° ′	° ′
Li	132 48	133 27	133 8
C	133 1	133 30	133 16
Na	133 56	134 38	134 17
Tl	135 8	135 15	135 12
Cd	135 25	135 44	135 35
F	135 42	136 11	135 57

Murmann and Rotter obtained 135° 42′ for the middle part of the spectrum.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	67 32	$1a$	90 14	76 14	76 16
	2	67 30	$2a$	90 11	76 14	
	3	67 36	$3a$	90 6	76 20	
C	1	67 30	$1a$	90 1	76 18	76 18
	2	67 29	$2a$	90 6	76 15	
	3	67 33	$3a$	90 0	76 21	
Na	1	67 21	$1a$	89 26	76 29	76 25
	2	67 17	$2a$	89 34	76 22	
	3	67 23	$3a$	89 39	76 24	
Tl	1	67 5	$1a$	89 0	76 30	76 28
	2	67 0	$2a$	89 4	76 24	
	3	67 7	$3a$	89 4	76 29	
Cd	1	66 56	$1a$	88 43	76 32	76 30
	2	66 50	$2a$	88 44	76 27	
	3	66 58	$3a$	88 49	76 30	
F	1	66 49	$1a$	88 28	76 35	76 33
	2	66 47	$2a$	88 31	76 31	
	3	66 45	$3a$	88 26	76 32	

Murmann and Rotter give 76° 52′ as the true optic axial angle, and state that $\rho < v$, which agrees with the order of the results above given for the various wave-lengths of light. Miller found $2V_a = 75° 49'$.

Dispersion of the Median Lines.—Determinations of the true optic axial angle $2V_a$ in toluene, the refractive index of which is almost identical with the mean index of the crystals of ammonium ferrous sulphate, afforded readings which indicated that the first median line is so dispersed in the symmetry plane that it is 9′ nearer to the axis a for red Li light than it is for greenish blue F light. This result is the mean of two determinations, which yielded the respective values 10′ and 8′. The inclined dispersion of the median lines is thus very small.

Effect of Rise of Temperature on the Optic Axial Angle.—Plate 2 was heated in the Fuess heating apparatus provided with the larger axial angle apparatus used in all these measurements, and the apparent optic axial angle in air, 2E, was found to diminish as the temperature rose. The following values were obtained for 60° C. (corrected with special precaution):—

Optic Axial Angle 2E at 60° C.

	°	′
For C-light	130	2
For Na-light	130	42
For Tl light...........	131	46

The apparent angle 2E thus diminishes by about 4° when the temperature is raised 50° C. (from 10° to 60° C.).

Comparison of the Optic Axial Angles of the four Salts of the Iron Group.—This is effected in the next table.

Optic Axial Angles $2V_a$ of the Iron Group.

	KFe sulphate.	RbFe sulphate.	CsFe sulphate.	AmFe sulphate.
	° ′	° ′	° ′	° ′
Li	67 1	73 24	75 2	76 16
C	67 2	73 23	75 0	76 18
Na	67 7	73 21	74 51	76 25
Tl	67 12	73 18	74 42	76 28
F	67 19	73 13	74 31	76 33

The optic axial angle of ammonium ferrous sulphate is thus slightly larger than that of cæsium ferrous sulphate, which is the largest of the optic axial angles of the alkali-metal salts. This was also found to be the case in the zinc double sulphate group, while in the corresponding zinc double selenate group the value for the ammonium salt was found to be slightly less than that for the cæsium salt. In all three groups the value for the ammonium

salt is thus in the proximity of that for the cæsium salt of the same group, sometimes on one side and sometimes on the other. The magnesium double sulphate, selenate, and chromate groups are not comparable, as the phenomenon of crossed axial-plane dispersion enters into those cases, and complicates them.

Summary of Conclusions.

Ammonium ferrous sulphate is a typical member of the monoclinic isomorphous series $R_2M\left\{\begin{matrix} S \\ Se \\ Cr \end{matrix}\right\}O_4)_2.6H_2O$. The clear, transparent, pale bluish-green crystals are distinguished from other members of the series by the exceptionally predominant development of the orthopinakoid of the second order $r'\{\bar{2}01\}$.

The same facts have been found to apply in this double sulphate iron group of salts of the series as were deduced from the previous investigations of the magnesium and zinc double sulphate and selenate groups,* namely, that the ammonium salt of any group is truly a member of the isomorphous series, but not eutropic with the potassium, rubidium, and cæsium salts of the group, which three latter salts are strictly eutropic with one another, and follow the rule of progression of the crystal properties with the atomic weight of the alkali metal.

The Crystal Angles.—Small but definitely measurable changes in the magnitude of the crystal angles occur when the potassium in potassium ferrous sulphate is replaced by ammonium, and they are mostly in the same direction as those which accompany the replacement of potassium by either rubidium or cæsium. Both the average and the maximum changes of interfacial angles for the ammonium interchange (for potassium) are almost exactly the same as for the replacement of potassium by cæsium, and twice as great as when rubidium is introduced instead of potassium (the average and maximum changes of angle being directly proportional to the atomic weights of the alkali metals). Also the monoclinic axial angle β (the axial angle *ac*, between the vertical and inclined axes) of ammonium ferrous sulphate is almost identical with that of cæsium ferrous sulphate.

The Morphological Axial Ratios of the ammonium salt are very similar to those of the analogous potassium, rubidium, and cæsium salts, and adequately so to prove true isomorphism in the usually accepted sense, that is, subject to the small variations of crystal angles referred to in the last paragraph.

The Volume Constants.—The molecular volume and topic axial ratios of

* 'Journ. Chem. Soc.,' 1905, vol. 87, p. 1123.

ammonium ferrous sulphate are very close to those of the rubidium salt of the group. *The molecular volume* of the ammonium salt is only one unit different (higher) from that of rubidium ferrous sulphate, whilst a difference of 9·8 units occurs between the volumes of the potassium and rubidium salts, and one of 13 units between those of the rubidium and cæsium salts of the group. The topic axial ratios, the expression of the molecular volume in the three dimensions of space, that is, the relative lengths of the edges of the parallelepipedal cell of the space-lattice, for the ammonium salt are very nearly the same as those of the rubidium salt, being as regards χ and ψ slightly higher, and as regards ω very slightly lower.

It is thus clear that the replacement of potassium by ammonium is accompanied by scarcely more volume or dimensional change than when rubidium is introduced instead of potassium. Consequently, the replacement of rubidium by ammonium, two metallic atoms Rb_2 by ten atoms of two ammonium radicles, $2NH_4$, is accompanied by scarcely any appreciable change of volume or of crystal-structure dimensions. This is a weighty conclusion from the point of view of the structure theory. On the other hand, the introduction of cæsium or potassium instead of rubidium causes a large volume and dimensional change. These results confirm the conclusions of a similar nature derived from the previous work on the magnesium and zinc groups.

Orientation of the Optical Ellipsoid.—Rotation of the optical ellipsoid about the symmetry axis occurs when one base is replaced by another in this iron group of salts, and the order of the rotation is: Ammonium salt, potassium salt, rubidium salt, and cæsium salt. The direction is forwards from the vertical axis, to which one of the axes (α or γ) of the ellipsoid is adjacent (only $8^\circ 42'$ removed) in the case of the ammonium salt.

Refractive Indices.—The whole of the refractive indices for all wavelengths of visible light, and also the mean index, of ammonium ferrous sulphate are near to and slightly higher than those of rubidium ferrous sulphate, and in no case so high as for the cæsium salt. Also the *double refraction* for the ammonium salt lies between the values of this constant for the rubidium and cæsium salts, but in this case nearer to the value for the cæsium salt.

The dimensions of the axes of the optical ellipsoid also lie between those for the rubidium and cæsium salts, and much nearer to those of the rubidium salt.

The Molecular Optical Constants.—The specific refraction and dispersion of the ammonium salt are much higher than those of the alkali-metal salts, which three latter salts arrange themselves as regards these constants in the

order of the atomic weights of the metals. The molecular dispersion of the ammonium salt lies between that of the rubidium and cæsium salts, and nearer to that of the latter.

The molecular refraction corresponding to each of the three refractive indices, and also the mean molecular refraction, $\frac{1}{3}(\alpha+\beta+\gamma)$, for the ammonium salt is very nearly the same as, and a very slight amount higher than, the corresponding value for the rubidium salt. All these results have been experimentally shown to be independent of the temperature.

Optic Axial Angles.—The optic axial angle of ammonium ferrous sulphate is slightly larger than the largest angle for the metallic salts, that of cæsium ferrous sulphate, and the dispersion, both of the optic axes and of the median lines in the symmetry plane, is small between the two extremes of the spectrum, and very similar for all four salts of the group.

Chief Conclusion.—The principal conclusion to be emphasised, as the result of this investigation, and in further confirmation of the deductions from the previous investigations of the zinc and magnesium groups of double sulphates and selenates, and those still more recently* derived from the study of the magnesium group of double chromates, is the following: The ammonium salts are truly isomorphous with the potassium, rubidium, and cæsium salts of this large monoclinic series of salts having the general formula $R_2M\left\{\begin{matrix}S\\Se\\Cr\end{matrix}\right\}O_4\Big\}_2.6H_2O$, but not eutropic with them, the three latter salts alone being eutropic (following the law of progression with atomic weight of the alkali metal) amongst themselves; also, it is a singular and very interesting fact that scarcely any change in structural dimensions occurs when ammonium and rubidium are interchanged for each other, that is, when ten atoms ($2NH_4$) replace two atoms (Rb_2), for they do so without appreciably altering the dimensions of the unit cell of the space-lattice.

* 'Mineralogical Magazine,' 1912, vol. 16, p. 169.

Studies of the Processes Operative in Solutions. XXVII.—*The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power.*

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Biot, the distinguished French physicist, to whose genius we owe the discovery, in 1815, of the property now spoken of as optical rotatory power, made the further discovery that certain substances in solution, notably tartaric acid, offer an exception to the rule that the deviation which a polarised ray undergoes in its passage through a liquid is greater the shorter the wave-length. The precise manner in which variation takes place was established by Arndtsen,* who determined the rotatory power of solutions of tartaric acid using light of the refrangibility of the lines *c*, D, E, *b*, F, *e* of the solar spectrum.

In calling attention to these observations, in the article "Light" in the third Supplement of Watts' 'Dictionary of Chemistry,' published in 1881, one of us pointed out (p. 1208) that—

> "Two optically active, chemically indifferent bodies of opposite rotatory power, having *different rotatory dispersive powers*, if mixed in certain proportions, would (as Biot has shown for a solution of dextrorotatory camphor in lævorotatory turpentine oil) exhibit phenomena similar to those manifested by tartaric acid solutions; hence the most probable explanation of the anomalous rotatory dispersive power of solutions of tartaric acid would appear to be that they contain, besides the acid, a compound of opposite rotatory power of the acid with water, in proportions varying according to the concentration and temperature of the solutions."

But that this explanation was not regarded as altogether satisfactory is apparent from a sentence written at about the same time which appears in the edition of Miller's 'Elements of Chemistry,' Part III, "Organic Chemistry" (p. 992), published in 1880:—

> "The anomalous rotatory dispersive power of aqueous solutions of tartaric acid almost necessitates the assumption that the acid forms a compound with water opposite to itself in rotatory power; the formation of a body having a reversed rotatory power as compared with that of the parent substance from a compound like dextrotartaric acid, which, according to Van't Hoff's hypothesis, has the constitution 2A—*i.e.*, is composed of two similar dextrorotatory groups—is, however, not easy to understand."

In those days, of course, our knowledge of structure was far less developed than is now the case. Meanwhile, notwithstanding the attention devoted to the study of optically active substances since the introduction of Van't Hoff's

* 'Ann. Chim. Phys.,' 1858, (3), vol. 54, p. 415.

masterly generalisation in 1875,* until recently it has been customary only to determine rotatory power in yellow light. The simplification and improvement of the polarimeter effected by W. H. Perkin, senior, who was the first to develop the method originally devised by Fizeau and Foucault in 1845, by using a spectroscopic eye-piece, undoubtedly gave an impetus to the use of light of other degrees of refrangibility. T. M. Lowry has since improved the method and by the use of photography has extended it so that the measurements can now be made without difficulty not only in the visible but also throughout the ultra-violet region;† this work, it may be added, was undertaken mainly in consequence of the suggestion made to him by one of us several years ago that it was desirable to reinvestigate the subject of anomalous rotatory dispersion from the point of view of Biot's suggestion.

The method has been in use during several years past in our laboratory and in that of Prof. Pope.

It is safe to say that it is no longer legitimate to confine the measurements of rotatory power to yellow light.

It is remarkable that so little attention should have been paid to rotatory dispersive power and to the anomalous behaviour of some substances. Walden, in his comprehensive survey of the subject of optical activity, in the lecture he delivered to the German Chemical Society in 1905,‡ mentions almost casually the abnormal behaviour of tartrates without reference to Biot's explanation and this has been disregarded also by Frankland, Patterson and other recent workers, even by Winther, who has discussed change in rotatory power particularly in relation to the changes in the "solution-volume" and the "internal pressure" of solutions.§ Winther, following Biot, considers that abnormalities in dispersive power are due to the presence of forms differing in rotatory power but supposes that these are complex molecules and compounds of solute and solvent.

The effect of solvents on the rotatory power of certain tartrates has been made the subject of most exhaustive study during the past 12 years by T. S. Patterson, who, in a series of 20 communications to the Chemical Society, has shown that different liquids produce extraordinarily different effects in changing the rotatory power especially of tartrates.

He has recently‖ summarised the results which he and others have obtained

* Compare Frankland, Presidential Address, 'Chem. Soc. Trans.,' 1912, p. 654.

† 'Phil. Trans.,' 1912, A, vol. 212, p. 261.

‡ 'Berichte,' pp. 366–408.

§ 'Zeit. Phys. Chem.,' vol. 60, pp. 563, 590, 641, 756.

‖ An attempt to harmonise qualitatively the relations between temperature and rotation for light of all refrangibilities of certain active substances both in the homogeneous state and in solution, 'Chem. Soc. Trans.,' 1913, p. 145.

but without arriving at any more definite conclusion as to the cause of the variations observed than that involved in the statement—

"it may be possible to explain all these facts in terms of the very popular, if somewhat vague—or because somewhat vague?—ideas, association or complex formation—solvation—and it would be exceedingly interesting if some exponent of these ideas would attempt to show that it is possible to formulate a consistent scheme based on them and capable of withstanding even the first breath of criticism but to the author it appears that the potentialities of the asymmetric carbon atom and of the most simple physical conception of those intermolecular forces to which liquefaction is due are ample to account for all the observed behaviour."

Apart from the difficulty of understanding what is implied in the expression "the potentialities of the asymmetric carbon atom and of the most simple physical conception of those intermolecular forces to which liquefaction is due," this pronouncement does not carry us very far.

The position is well summarised in the December number of the Chemical Society's 'Transactions" (p. 2313), by Pope and Winmill, in the following statement:—

"It may here be noted that the variability of rotation constants with solvent was attributed by Pope and Peachey ('Trans.,' 1889, vol. 75, p. 1111), in the main, to changes in association of the optically active substance produced by the solvent; Patterson opposed this view ('Trans.,' 1901, vol. 79, p. 186) and strongly advocated the idea that the cause of variation of rotation constant with solvent is to be found in variation of the internal pressure prevailing in the solution. Patterson's later papers indicate that he has abandoned the view that internal pressure is an operative factor in connexion with variations in the rotatory power, whilst Walden ('Ber.,' 1905, vol. 38, p. 345) apparently adopts the view, that, in the main, the association factor determines the rotatory power. The complex character of the problem under discussion discourages any attempt to draw a final judgment between the several views which have been advanced as guides to further investigation."

It has long been obvious that the inquiry into the processes operative in solutions which is the subject of this series of studies would be incomplete if changes in optical rotatory power such as have been referred to were not considered. The observations recorded in the previous communication of the series (XXVI),* in which the passage from the lævorotatory to the dextrorotatory form of fructose is discussed, have so direct a bearing on the problem that we have been led to give the matter special consideration.

In considering the literature of the subject, our attention was at once attracted by a recent account given by Pope and Winmill (*loc. cit.*) of the optical properties of tetrahydroquinaldine and various derivatives of this compound. It is pointed out by these authors that the orthonitrobenzoyl-derivative has quite abnormal rotatory constants and that its rotatory

* "The Disturbance of the Equilibrium in Solutions of Fructose by Salts and Non-electrolytes," by E. E. Walker, 'Roy. Soc. Proc.,' 1913, A, vol. 88, p. 246.

dispersive power is anomalous; the mean values for the latter which they record are as follows:—

Table I.

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg green/Na yellow	−0·1181	+1·701	−1·218	+0·483
Hg yellow/Na yellow	+0·805	+1·147	+0·4995	+0·917

It will be observed that the variation in the dispersion coefficient brought about by a change of solvent is very great. 2-Nitrotoluene-4-sulphonyl-tetrahydroquinaldine is equally abnormal in its behaviour; moreover, in the case of this compound, benzene has most and acetone least effect on the rotatory power, which is a complete reversal of the order of effect observed in the case of nine other derivatives similar to these two compounds which were studied; these behave normally, though the rotatory power of each varies greatly according to the solvent used: in the case of each compound the rotatory dispersive power is the same whatever the solvent used. It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned.

Discussion of Special Cases and Construction of Characteristic Rotation-Dispersion Diagrams.

The optical properties of a liquid substance or of a solution consisting of two isodynamic forms of different rotatory power may be represented graphically in a very simple manner, as shown in fig. 1, in which the following four cases are represented:—

Case I. Two substances having rotatory powers of the same sign and the same dispersive power.

Case II. Two substances having rotatory powers of the same sign but different dispersive power.

Case III. Two substances having rotatory power of opposite sign but the same dispersive power.

Case IV. Two substances having rotatory power of opposite sign and also different dispersive powers.

In the diagram, specific rotatory power is represented by the ordinates and percentage composition by the abscissæ. It is assumed that the rotatory power of each of the two constituent isomers is constant under all conditions; the extent to which this assumption is justifiable will be discussed later on when various actual examples have been considered.

R_1, G_1, B_1, represent the specific rotatory power of the one form on using red, green and blue light respectively, R_2, G_2 and B_2 have the same significance for the isomeric form. The diagrams are self-explanatory. It is only necessary to point out that only compounds coming under Case IV are likely to occasion anomalous dispersion; the region in which the dispersion is anomalous lies between the two dotted lines in the diagram.

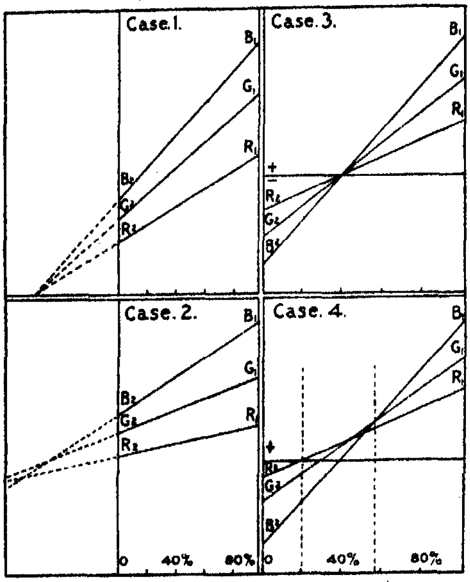


FIG. 1.—Rotation-composition diagrams.

Fructose.—Passing from ideal cases to actual facts, the case of fructose may now be considered. There is every reason to suppose that this compound is present in solution in two isodynamic forms and it has been shown in Part XXVI of these studies that the proportions in which these are presumably present in equilibrium may be altered to a considerable extent by the addition of alcohol or other substances. In order to determine under which of the above four cases fructose comes, a solution was made up containing two molecular proportions of fructose and 100 molecular proportions of water and the rotatory power of this solution was determined using the light of the yellow, green and blue lines emitted by a mercury vapour lamp. Various quantities of alcohol (containing 0·73 per cent. water) were then added and the specific rotatory powers determined as before. The results are given in Table II.

It will be noticed that the values given in the last two columns representing the dispersion are practically constant, except in the most dilute solution in which the experimental error is large.

This result is of importance in proving that the dispersion may be normal even when more than one form is present, a conclusion of moment as Winther appears to consider that when the dispersion does not vary it is to be supposed that only one substance is present in solution; in such cases he ascribes the changes in rotatory power merely to the alteration of the internal pressure.

Table II.

Molecular proportions of alcohol per 100 of water.	α_{Yellow}	α_{Green}	α_{Blue}	$[\alpha]_Y^{25}$	$[\alpha]_G^{25}$	$[\alpha]_B^{25}$	$\frac{\alpha_G}{\alpha Y}$	$\frac{\alpha_B}{\alpha_G}$
0·00	−66°·503	−75°·230	−124°·88	−93°·73	−106°·08	−175°·29	1·1312	1·653
9·28	49·557	56·080	92·56	87·08	98·55	162·65	1·1316	1·651
24·65	34·279	38·794	64·15	80·13	90·69	149·62	1·1317	1·654
54·9	20·908	23·654	39·10	73·50	83·17	137·48	1·1316	1·653
167·0	9·059	10·255	16·98	64·22	72·52	120·59	1·1322	1·656
1724·0	0·700	0·786	1·32	49·7	55·7	93·7	1·12	1·68

The values for blue light cannot be regarded as so nearly accurate as those for yellow and green; on account of the spectroscope being in the eye-piece of the polarimeter, the flood of yellow and green light is so great that when the rotation is considerable the blue is obscured. Therefore in the case of solutions 1 and 2, a blue filter was used to cut out the yellow and green bands; unfortunately this rendered the blue fainter also.

If the assumption be made that the composition of the mixture studied is a linear function of the specific rotatory power in the case of a given coloured light, all the points representing the specific rotatory power in other colours should fall on straight lines when placed on the appropriate ordinates; the abscissæ should then represent the composition to an unknown scale. To construct the diagram characteristic of a substance, a *reference line* is drawn with a slope of unity and on this are plotted the various specific rotations of light of any one of the refrangibilities observed. The points for other refrangibilities are then plotted on the ordinates passing through the points previously located on the reference line. The observations may be those made either at different temperatures or in different solvents or at different concentrations.

It is proposed to call the portion of the rotation-composition diagram drawn in the manner described the *Characteristic Diagram*, as it shows under which of the cases discussed on p. 391 the substance comes.

When the characteristic diagram of fructose (fig. 2) is drawn from the data given in Table II, it is clear that this sugar comes under Case III and that it is to be supposed therefore that the two isodynamic forms have the

same dispersive power. Glucose, in all probability, would come under Case I, as both the α and β forms are positive and presumably equally dispersive.

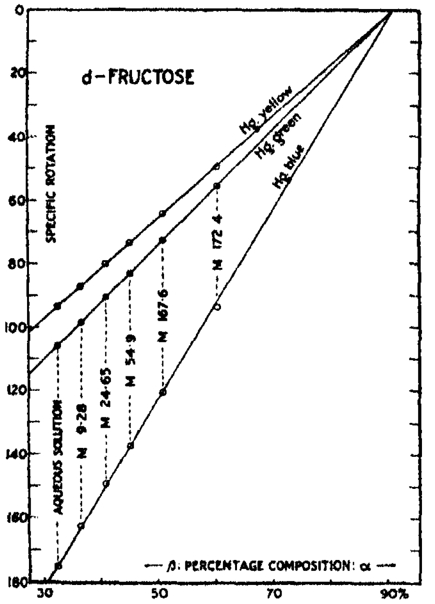


FIG. 2.—Characteristic diagram of *d*-Fructose. Equilibrium between α and β forms altered by the addition of alcohol to the aqueous solution. Reference colour, Hg green.

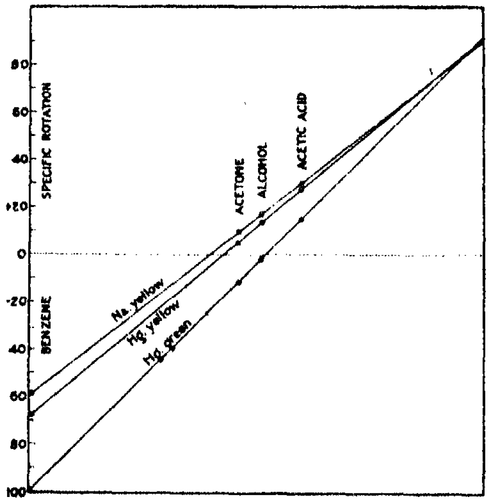


FIG. 3. — *o*-Nitrobenzoyl-l-tetrahydroquinaldine. Equilibrium varied by change of solvent at constant temperature 20° C. Reference colour, Hg green.

In cases in which the rotatory powers of the separate forms are unknown the composition cannot be inferred; but in a case such as that fructose affords it is possible to attach a scale to the axis of abscissæ, assuming that the rotatory power of each form is the same at all dilutions.

According to Hudson, the specific rotatory power of the two forms of fructose are $[\alpha]_D = +17°$ and $-140°$. The corresponding mercury green values deduced by extrapolation from the dispersion curve may be taken as $+20°$ and $-165°$. Using these values, the rotations in green light corresponding to various percentages may be directly calculated.

Any substance which has a variable rotatory power but constant dispersive power would be represented by a similar diagram.

o-Nitrobenzoyltetrahydroquinaldine.—The mean specific rotatory powers of this substance in various solvents are as follows:—

Table III.

Solvent.	$[\alpha]_D$	$[\alpha]_{Hg\ yellow}$	$[\alpha]_{Hg\ green}$
Alcohol	+ 2°·017	+ 13°·77	+ 17°·11
Benzene	−99·30	−66·97	−58·37
Acetone	−11·73	+ 4·83	+ 9·67
Acetic acid	+ 14·50	+ 27·50	+ 30·00

The characteristic diagram (fig. 3) constructed from these data and the dispersion values previously cited shows that this substance is to be regarded as coming under Case IV. The slope of the lines is no longer a measure of the dispersion as it is in the case of fructose but gives what is practically identical with Winther's "solution dispersion coefficient."*

The value of this coefficient calculated from the various pairs of solutions is remarkably constant in comparison with the apparently irregular variation of the dispersion coefficient (*cp.* Tables I and IV).

Table IV.

	$\dfrac{\Delta[\alpha]_{Hg\ green}}{\Delta[\alpha]_{Hg\ yellow}}$	$\dfrac{\Delta[\alpha]_{Hg\ green}}{\Delta[\alpha]_{Na\ yellow}}$
Alcohol and benzene	1·215	1·289
Acetone and benzene	1·220	1·287
Acetic acid and benzene	1·232	1·288
Acetic acid and alcohol	1·232	1·281
Point of intersection	84·8°	83·7°

* Winther ('Zeit. Phys. Chem.,' vol. 41, p. 207) has shown that the increase in the rotatory power of the ethereal salts of tartaric acid can be represented as a parabolic function of the temperature

$$[\alpha] = a + b(t - 149).$$

If b_1 and b_2 are the values of b for light of two different wave lengths, then Winther called the ratio b_1/b_2 the rational dispersion coefficient; this was shown to be to a large extent independent of the concentration and the solvents. Subsequently, he (*ibid.*, vol. 45, p. 373) used what he termed the "solution-dispersion coefficient"; this was calculated from the expression :—

$$\Delta[\alpha]_a/\Delta[\alpha]_b$$

where $\Delta[\alpha]_a$ and $\Delta[\alpha]_b$ are the changes in rotatory power of light of two different wave lengths occasioned by a given change in concentration. (The "rational dispersion coefficient" was determined from a similar expression when the constants of the parabolic equation were not known.)

It is clear that this latter ratio is identical with the ratio of the slopes of the lines of the characteristic diagram; in fact the slope of these lines represents this quantity

Methylic Tartrate.—Methylic tartrate may be taken as a third example. Probably more work has been done on the rotatory power of the ethereal salts and other derivatives of tartaric acid than of any other group of compounds; there are therefore ample data for purposes of discussion: nevertheless it was thought desirable to make a set of experiments similar to those made with fructose, in order to compare the effects produced in the two cases. The rotation was measured in the yellow, green, blue-green and blue light of the mercury lamp spectrum; it was impossible to measure the blue-green very accurately on account of its extreme faintness but the values show the trend of the curve sufficiently well and are included in the diagram. The solution contained 1 gramme molecular proportion of tartrate to 100 of water and the number of gramme molecules of alcohol recorded in the table.

Table V.

Molecular proportions of alcohol per 100 of water.	α_{Yellow}	α_{Green}	$\alpha_{Blue\text{-}green}$	α_{Blue}	$[\alpha]^{25}_{Y}$	$[\alpha]^{25}_{G}$	$[\alpha]^{25}_{BG}$	$[\alpha]^{25}_{B}$
0·00	+7°·676	+8°·443	+9°·77	+11°·32	+19°·01	+20°·91	+24°·19	+28°·04
8·91	5·494	6·025	6·86	7·95	16·28	17·85	20·32	23·55
22·20	3·487	3·778	4·29	4·60	12·56	13·61	15·45	16·57
52·0	1·758	1·865	2·06	1·94	10·60	11·23	12·42	11·70
128·8	0·650	0·673	0·65	0·43	7·51	7·76	7·51	4·96

The characteristic diagram (fig. 4) drawn from these data shows that methylic tartrate also comes under Case IV. The comparatively low values at which the lines cross is probably an indication that there is considerably less difference between the magnitude of the dispersion of the two forms than in the case of the quinaldine derivative and probably also a correspondingly smaller difference in constitution.

A point of great significance in this diagram is the fact that the values for the ethereal salt alone at various temperatures lie practically on the projection of these curves, the whole forming one complete diagram. These values were deduced from Winther's data* by graphic interpolation from the dispersion curves; the values so obtained are given in Table VI.

directly when the line of unit slope is chosen as denominator. It therefore appears desirable to designate the ratio :—

$$\Delta[\alpha]_a/\Delta[\alpha]_b$$

by a single term, whether the change in equilibrium be caused by an alteration either in temperature or in concentration or solvent; for this purpose the term "rational dispersion coefficient" might well be retained.

* *Op. cit.*, vol. 41, p. 176.

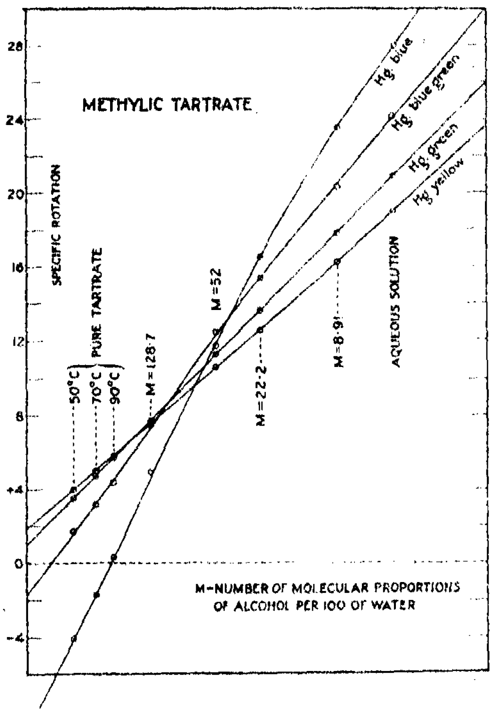


FIG. 4.—Equilibrium varied by the addition of alcohol to the aqueous solution and by heating the original substances.

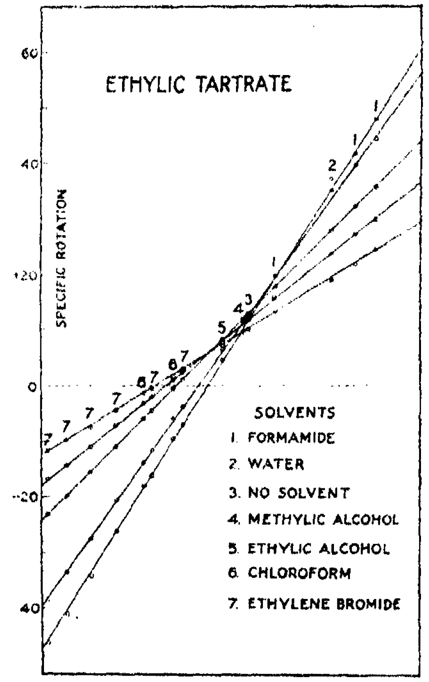


FIG. 5.—Ethylic tartrate. Equilibrium varied by change of solvent and concentration at constant temperature 20° C.

Table VI.

Temperature.	$[\alpha]^t_Y$	$[\alpha]^t_G$	$[\alpha]^t_{BG}$	$[\alpha]^t_B$
° C.				
90	+5°·88	+5°·72	+4°·43	+0°·34
70	5·06	4·78	3·26	−1·68
50	4·02	3·54	1·74	−4·03

Ethylic Tartrate.—Fortunately Winther has supplied very complete data for this substance.* The characteristic diagram is given in fig. 5; some of the points have been omitted, as they come so close together. Excepting those for solutions in water, the values all lie very close indeed to straight lines. The solution in benzene (not included) also appears to afford slightly exceptional values.

2-*Nitrotoluene-4-sulphonyltetrahydroquinaldine.*—The characteristic diagrams

* *Op. cit.*, vol. 60, p. 582.

of this substance are given in fig. 6. It will at once be obvious that it differs in a marked degree from those previously constructed and does not correspond with any of the ideal cases that have been discussed. Apparently, in solutions of this substance, the dispersion is not a function of the rotatory power and there is a second independent variable concerned.

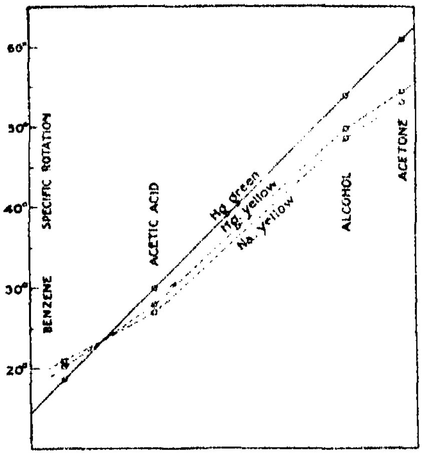
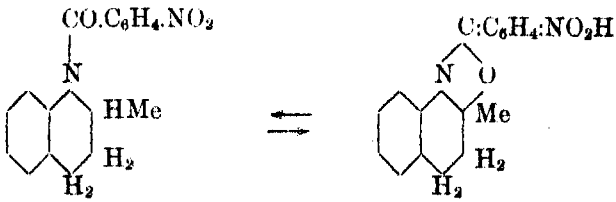


FIG. 6.—2-nitrotoluene-4-sulphonyl-1-tetrahydroquinaldine. Equilibrium varied by change of solvent at constant temperature 20° C.

An Explanation of Anomalous Rotatory Dispersive Power.

The question to be considered is what two substances of opposite rotatory power and different rotatory dispersive power are likely to exist in cases such as those under consideration. Taking into account the views one of us has long held in regard to the origin of colour, as orthonitrobenzoyltetrahydroquinaldine is a yellow substance, it appears not improbable that it may exist in solution in two isodynamic forms, viz.:—



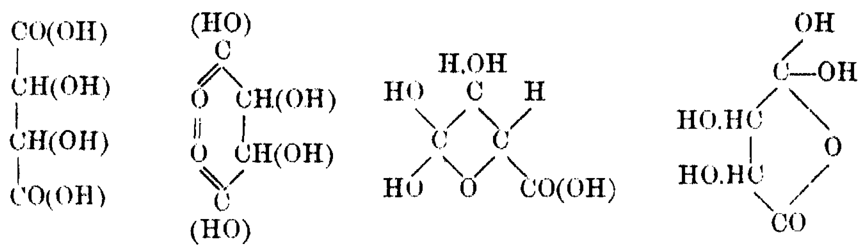
Being quinonoid, the second of these would doubtless be the more dispersive.

Passing to tartaric acid, we have to account for the fact that the rotatory power of the acid and of its ethereal salts is more or less affected by variation in the temperature; morever, that not only water but also "neutral" solvents

modify this rotatory power, often to a considerable extent; and that the rotatory dispersive power of the solutions is generally anomalous. According to Biot, no such abnormal dispersive power is noticeable in solutions of the metallic tartrates; this statement has been confirmed by Winther.

Although it has been customary to regard carboxylic acids as compounds containing the free carboxylic radicle, the evidence that such is always the case is in no way sufficient, let alone conclusive. The behaviour of monocarboxylic acids, especially their recognised tendency to form double molecules, as in the case of acetic acid, is clear proof that the carboxylic radicle is far from being saturated.

Taking into account the views that now prevail that valency has direction and the conclusion which is the outcome of this conviction that carbon atoms are not united as mere links in a chain but tend to form re-entering systems, such systems being formed preferentially from either five or six atoms; moreover, that oxygen atoms may take the place of carbon atoms: it is both possible and probable that the fundamental molecule of tartaric acid can exist not only in the "open" form commonly pictured (I) but also in various isodynamic "closed" forms (II, III and IV):—



I. II. III. IV.

It cannot be denied that there is little to guide us in choosing between these formulæ or in deciding which is the most likely form to preponderate.*

The third obviously bears a marked resemblance to that of fructose—in which, in place of the four-membered (tetraphane) ring there is a five-membered (pentaphane) ring. The fourth is similar to the third.

It is scarcely probable, we think, either that any alteration in the degree of hydration of a substance represented by formula I or that the passage from

* It is remarkable that possibilities such as these have not been taken into account by Walden, who has recognised that structural changes may in some cases underlie the alterations in rotatory power observed in solutions (*op. cit.*, p. 407). Taking the ethereal salts of tartaric acid as an example, he has postulated changes which appear to us not only to be improbable, but altogether insufficient to account for the magnitude of the effects observed, especially the change in sign of the rotatory power, accompanied by a sufficient difference in dispersive power to give rise to the phenomenon of anomalous

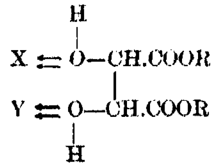
form I into form II would be attended with an alteration in the sign of the rotatory power such as is known to take place in solutions of tartaric acid; and on general grounds the second is scarcely a probable form.

We believe the known facts are best accounted for on the assumption that forms I and III are the two modifications in equilibrium in most cases and that form III is the more stable at lower temperatures and in concentrated solutions, the carboxylic form at higher temperatures and in weaker solutions: if this be the case, the lactonic form is the more dispersive and of lower rotatory power.

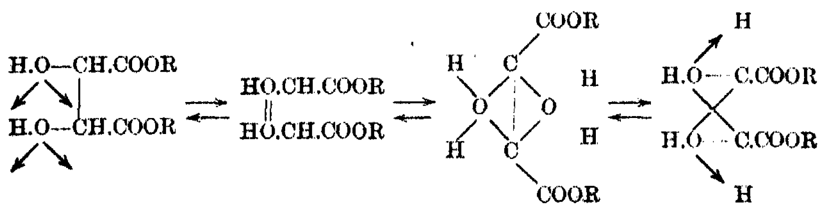
It is to be expected that metallic salts would exist as carboxylates: the normal behaviour of metallic tartrates is therefore such as might be expected from the point of view of our hypothesis.

Form IV appears to us to be less probable than III on various grounds.

dispersion. The changes which Walden pictures as possible are conveyed by the following symbols:—



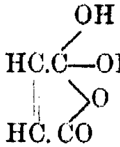
(X and Y may be either other molecules of the tartrate or molecules of the solvent.)



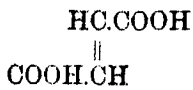
It is well known that gluconic and similar acids derived from the sugars are very readily converted into the corresponding lactones—a change precisely similar to that attending the conversion of the carboxylic form of tartaric acid into the tetraphane form; and if gluconic lactone be regarded as present in solution in a hydrated form, the behaviour of the two acids is in correspondence. Gluconic and similar lactones, moreover, have high rotatory powers, whilst the acids derived from them have low rotatory powers of opposite sign—which is precisely the difference we have postulated in the case of the two isodynamic forms of tartaric acid.

It may also be pointed out here that in the case of the ethereal salts of tartaric acid two stereoisomeric modifications of the tetraphane and pentaphane forms are possible: this is also true of the quinonoid form of the *o*-nitroquinaldine derivative examined by Pope and Winmill. As "asymmetric influences" are likely to be operative in such cases, the proportions in which the two isomerides are in equilibrium may be very different and one form prevail to the almost entire exclusion of the other.

A similar formula has been suggested for maleic acid in contradistinction to the dicarboxylic formula assigned to the isomeric fumaric acid

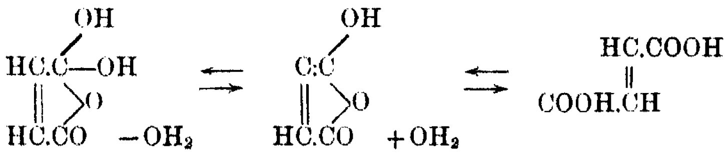


Maleic acid.



Fumaric acid.

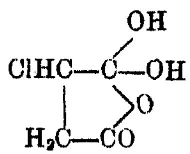
Such a formula is justified not only by the fact that maleic and fumaric acids differ considerably in strength but especially because maleic acid is converted into fumaric acid by mere contact with chlorhydric or bromhydric acid—a change which is easily accounted for by the assumption of this formula but with difficulty in any other way.



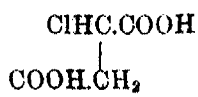
If therefore tartaric acid existed in form IV under ordinary conditions, it is to be expected that it would be easily converted into its optical isomeride; actually this change only takes place under special conditions and at relatively high temperatures.

Malic acid resembles tartaric acid in its optical behaviour and a similar explanation may be given of its peculiarities. It is in accordance with our hypothesis that the rotatory power of methoxysuccinic acid, $COOH.CH_2.CH(OMe).COOH$, is subject to but slight variation, as the formation from this compound of a closed tetraphane system corresponding to form III of tartaric acid is impossible; it is nevertheless conceivable that the two compounds *in esse* in the original substance may both give rise to the corresponding derivative: but this argument would not apply to the case of chlorosuccinic acid, for example.

In this latter case, however, two forms are still possible, related to one another as are maleic and fumaric acids, viz.,



I.



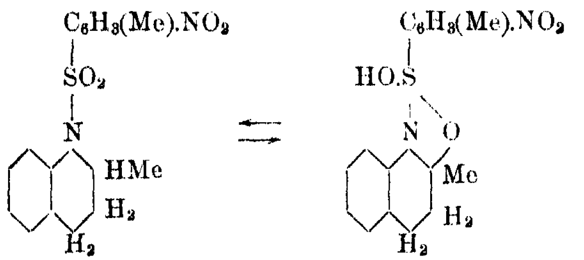
II.

It is well known that the acid chloride derived from succinic acid has a

constitution corresponding to formula I and it is by no means improbable that a solution of the acid in large part consists of molecules of this type.

It is obvious that much may yet be learnt by the thorough optical study of active derivatives of succinic acid and by contrasting their optical characters with their behaviour as acids.

The exceptional behaviour of the orthonitrotoluenesulphonyl-derivative described by Pope and Winmill may be explained on the assumption that it undergoes change into an isomeric form, of which two stereoisomeric modifications are possible.



The hypothesis now advocated may be applied in other cases, for example, perhaps in explanation of the great difference in rotatory power of the ortho-substituted derivatives of menthylic alcohol in comparison with the isomeric meta- and para-compounds and of similar differences among the glycerates.

In view of the well known fact that the rotatory power is often considerably affected by the solvent, it may appear surprising that diagrams should be obtained which are so closely in accord with the assumption we have made that only two optically active constituents are in equilibrium and that these have constant rotatory power. Although an irregular or sudden variation in the rotatory power of any component of the solution would inevitably give rise to corresponding irregularities in the characteristic diagram if the substance came under cases II or IV, the variation might not be apparent if the factors influencing the equilibrium were equally concerned in the changes in rotatory power.

The result at which we have arrived—that if the rotatory power of a substance in solution be observed, whatever the variation in the conditions, the observations in light of any particular refrangibility, as a rule, can all be located upon the same straight line in the characteristic diagram—appears to us to be of deep significance, as indicating a relationship among solvents generally, underlying their action towards substances generally, of a very definite and regular character: each solvent would appear to have its definite

sphere and mode of action, so that any two solvents behave relatively always in the same way towards solutes generally, apart from the exceptional cases in which some special property of the solute comes into operation to disturb this regularity of action.*

It is noteworthy that although the rotatory power of each substance varies considerably in ten of the twelve cases brought forward by Pope and Winmill the dispersive power of each set of solutions is practically identical.

By considering the behaviour of solvents generally and by further study of cases such as that afforded by the orthonitroparasulphonyl-derivative frequently referred to, in which case the activity of benzene as a solvent is quite out of the normal order, we hope that we shall be able to throw further light on this part of our subject. But taking into account the numerous factors involved, the equilibrium arrived at in each case cannot well be otherwise than the outcome of a variety of changes which balance one another. It is not likely, therefore, that a simple solution of the problem can be found. The difficulty is all the greater because of the difficulty of arriving at any proper basis of comparison. Hitherto it has been customary to contrast the values arrived at by observations made in light of the refrangibility of the sodium line but this is obviously insufficient; even, however, when the observations are extended to rays of other refrangibilities, it is possible that the difficulty of making proper comparisons met with in the case of other physical properties will still not be overcome.

To state our views, in a few words:—

The variations in rotatory power met with in optically active compounds may be ascribed (*a*) to alterations in molecular size and to the formation of compounds between solvent and solute; (*b*) to the occurrence of changes giving rise to the presence of reversibly related isodynamic forms.

The changes included under (*a*) are common to all optically active substances; those included under (*b*) can occur only in special cases. In these special cases, if the change involve the formation of compounds so different in chemical type that they not only differ in rotatory power in sign but also in rotatory dispersive power, the product might have anomalous dispersive power; in other cases, it would behave normally.

* *Cp.* Winther, *op. cit.*, vol. 60, p. 702; Walden, *op. cit.*, p. 397.

On the Luminosity Curves of Persons having Normal and Abnormal Colour Vision.

By W. WATSON, D.Sc., F.R.S.

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§ 1. When reading a recent paper before the Royal Society, and also in the Press, Dr. Edridge Green has stated that he can find no connection between the luminosity and the colour sense of persons having either normal or abnormal colour sensations. Since I feel that to allow such a statement to go unchallenged might be interpreted as meaning that no such connection could be shown to exist, I propose in the following paper to place before the Society some of the evidence which indicates that there is in reality a very intimate relation between luminosity and colour sense. The results given include a small part of those which have been obtained in a series of experiments which have occupied the last two years and form part of an investigation which is still in progress.

The term "luminosity" as used in this paper has the following meaning: Suppose that light from some source, such as the electric arc, is admitted to a spectroscope by means of which a real pure spectrum is produced, and that a slide in the plane in which the spectrum is formed carries a slit of fixed width. Light of sensibly one wave-length, *i.e.* monochromatic light, will pass through this slit, and by means of a lens placed in the beam of this light an image of the first face of the prism which is used to form the spectrum can be formed on a screen. In this way a monochromatic patch of light is obtained, the brightness of which depends on the nature of the source of light, the width of the collimator slit, the width of the slit placed in the spectrum, which for short will be called the movable slit, and the dimensions of the lenses employed. Further, if alongside this coloured patch is formed a white patch of light produced by light which proceeds from the same source but has not undergone dispersion, and that by some means or other the intensity* of this white light is altered till the coloured and white patches appear to the eye equally bright, then the intensity of the white light, measured in any arbitrary units, measures the luminosity of the light of that colour which is passing through the movable slit. Since the unit in which the white light is measured is arbitrary, we are not concerned

* The physical brightness of a light, *i.e.* the stimulus, will be spoken of as the ntensity, the term brightness being reserved for the sensation produced when the light nters the eye.

with the absolute intensity of illumination of the white patch, and may use any device we like to alter the quantity of white light which falls on the screen so long as we are able to measure the ratio of the quantity of light employed in different experiments. It will further be observed that for any given person the measurement of the luminosity of a given coloured light in the spectrum involves the comparison of the brightness of the coloured patch as it appears to him with the brightness of the white patch as it appears to him.

The above definition of what is meant by the luminosity of a colour in the spectrum of a given source is equivalent to that employed by Sir William Abney in all his work, and the only reason for giving it is that to follow the reasoning used in this paper it is essential that this definition should be kept in mind. A convenient arrangement for conducting measurements of luminosity has been described by Abney and Festing,* and has been employed in making the observations given below.

This is hardly the place to discuss the accuracy with which we are able to judge of the comparative brightness of, say, a white and a green light. It is admittedly a difficult operation, but the results which are quoted below show that if the conditions are suitably chosen the measurement can be performed with considerable consistency. The difficulty of comparing the brightness of a coloured light with that of a white light is almost completely obviated if a flicker method is employed, in which the coloured and white lights are made to successively occupy the same spot on the screen and the intensity of the white is altered till the flicker vanishes. If suitable precautions are taken even quite inexperienced observers are found to be capable of making quite consistent measurements by the flicker method, and a satisfactory piece of apparatus for such measurements is described later.

If the movable slit described above is placed in different parts of the spectrum and the intensity of the white which appears equally bright is measured in each place, on plotting these intensities as ordinates, the abscissæ being prism deviations, a luminosity curve is obtained, that is a curve which gives the luminosity of the different colours in the spectrum of the source and for the particular prism employed.

As has been mentioned, the unit in which the intensity of the white is measured is quite arbitrary, and throughout this paper it is taken as such that for a normal eye the maximum luminosity in the spectrum of the brightness employed is 100.† The abscissæ of the luminosity curves given are also

* 'Phil. Trans.,' 1886, Part II, p. 455.

† The intensity of illumination of the screen corresponding to 100 is throughout about 5 lux, or 0·5 candle-feet.

expressed in arbitrary units which are proportional to the deviations produced by the prism system, and for convenience of reference to Sir William Abney's published measurements the unit employed is the same that he uses. The connection between these standard scale readings, which will be indicated by the letters S.S.N., and the wave-lengths are given in Table I. It would be possible to reduce the results so as to make them correspond to a normal spectrum, *i.e.* a grating spectrum, when they would be independent of the dispersion curve of the particular prism employed. Since, however, we shall only be dealing with the differences of the luminosity curves obtained by different persons it seems hardly necessary to go through the somewhat laborious calculations involved.

Table I.

Scale number.	Wave-length.	Scale number.	Wave-length.
S.S.N.	Å.U.	S.S.N.	Å.U.
62	6957	44	5481
60	6728	42	5373
58	6521	40	5270
56	6330	38	5172
54	6152	36	5085
52	5996	34	5002
50	5850	32	4924
48	5720	30	4848
46	5596	28	4776

Suppose that when making a set of observations we start with the movable slit at the extreme red end of the spectrum and determine the intensity w_1 of the white which appears of the same brightness as the colour and then move the slit towards the blue through a distance equal to its width and again determine the intensity w_2 of the white, and so on throughout the spectrum. We should in this way determine piece by piece the brightness of the whole spectrum, and the sum $w_1+w_2+w_3+$, etc., could be taken to represent the total brightness of the whole spectrum. If now the slide carrying the slit were removed, so that the light corresponding to the whole spectrum was allowed to fall on the same portion of the screen, thus forming white, and we now determine the intensity W of the comparison white which is equal in brightness to this recombined spectrum. Then it has been shown by Abney, Tufts, Ives and others* that

$$W = w_1+w_2+w_3+, \text{ etc.}$$

* This statement requires a certain amount of limitation, and must be held only to apply to spectra of moderate brightness and to sources of light such that the light is not chiefly due to the blue and violet. The proposition that the luminosity of the sum of two lights is equal to the sum of the separate luminosities does not apply to very bright lights, and in the case of very small intensities may not apply in the blue and violet.

That is, the luminosity of the recombined spectrum is equal to the sum of the luminosities of its parts.

Now the sum $w_1+w_2+w_3+$, etc., is proportional to the area enclosed by the luminosity curve. Hence the area of the luminosity curve represents the total brightness of the light which is formed into the spectrum and is, therefore, a constant whatever the condition of the vision of the person who makes the observations. This is at once apparent if we remember that if the brightness of the whole recombined spectrum is compared with the comparison white, since these whites are derived from the same source and must, therefore, have exactly the same composition, a setting which appears correct to one person must also appear correct to any other, whatever the differences which may exist between their vision.

The fact that with a given spectroscope and source of light, if the scale used for measuring the white is the same for all measurements, the area of the luminosity curve will be always the same is of great utility, since it allows us to correct for any variation in the unit in terms of which the white is measured, such as may occur owing to the mirrors, lenses, etc., becoming tarnished. It may be mentioned here that when a colour-blind observer makes a luminosity-curve determination I have often obtained my own curve at the same time. The two sets of measurements being made immediately one after the other there is no time for the instrument to alter, and the areas of the curves obtained have always been the same, although the shapes of the curves are often entirely different.

§ 2. *Calculation of the Form of the Luminosity Curve for Colour-Deficient Observers.*—Before giving the luminosity curves obtained in the case of colour-deficient observers, it will be convenient to calculate what would be the form of the curves on certain assumptions. We shall then be in a position to judge of the accuracy of these assumptions by comparing the calculated curves with those obtained by observation.

Starting from the well-established fact that all colours can be matched by a combination, in suitable proportions, of three properly selected colours, Thomas Young and Helmholtz developed a theory of colour vision which supposes that the machinery by which colour is perceived consists of three sets of mechanism, and that the sensation produced by light of any colour is the sum of the sensations due to the individual mechanisms. Or, as we may say, the sensation produced is the sum of the separate sensations produced by these separate mechanisms.

It is hardly necessary here to consider the line of reasoning by which the amount of each sensation produced by the different colours of the spectrum can be derived from experiments in which a coloured light of one wave-

length is matched by the mixture of lights of two other wave-lengths. Suffice it to say that Koenig and Abney have published curves which give for each wave-length the values of the three sensations. These three sensations are generally referred to as the red, green, and blue sensations. These names are rather unfortunate, as persons unfamiliar with the subject are apt to suppose that the green sensation, say, is alone operative when green light enters the eye. As a matter of fact, in the case of a normal eye, all three sensations are affected by green light. The extreme red is the only part of the spectrum which affects but one of the mechanisms.

Given the luminosity curve for any given source of light, and making use of Abney's values* for the ratio of the ordinates of the three sensation curves for the different spectral colours, we can construct three sensation curves such that for any wave-length the sum of the ordinates of the three curves is equal to the ordinate of the luminosity curve. In this way we obtain the sensation curves in terms of luminosity, and the thin line curves given in fig. 1 are Abney's curves for the crater of the electric arc, the thicker line curve being the corresponding luminosity curve.

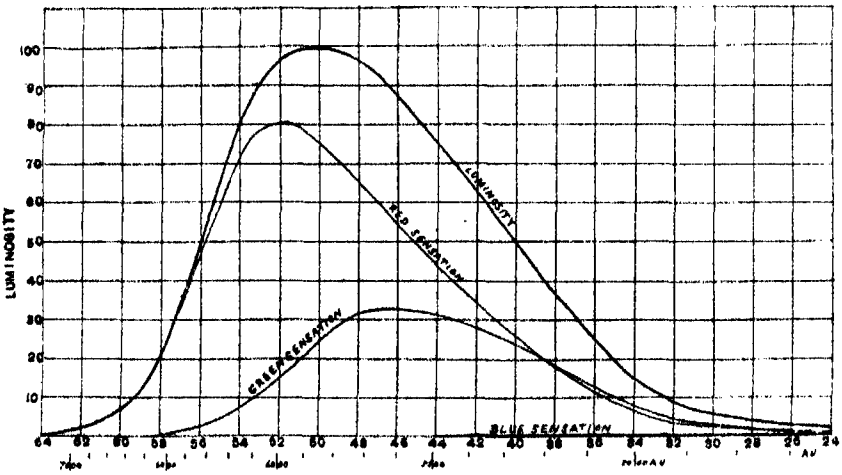


FIG. 1.

When white light, that is light of all wave-lengths, enters the eye, the effect produced on the three receptive mechanisms will be proportional to the areas of the three sensation curves. The relative areas of these curves for the electric arc are:—

Area of red sensation curve	579
Area of green sensation curve	248
Area of blue sensation curve.........	3·26

* 'Phil. Trans.,' 1905, A, vol. 205, p. 333.

We have now to consider the manner in which the sensation curves of a person who has defective colour vision differ from the normal. In several papers, Abney has brought forward evidence that, at any rate, in the case of the more ordinary forms of colour defect, either the red sensation curve or the green sensation curve is modified, and that this modification is such that the shape of the curve remains unaltered, each ordinate being reduced in the same proportion.* Thus, if the red sensation is deficient, and, say, the ordinate of the red sensation curve for any given wave-length is half the corresponding ordinate for the normal, then for all other wave-lengths the ordinates of the red sensation curve are also half those of the normal red sensation curve. Hence it follows that the area of the red sensation curve must also be half the area of the corresponding curve for the normal.

If we possessed any method of measuring in absolute units the sensation produced when light of a given intensity enters the eye, we should be able to tackle the question as to whether the maximum ordinate of the sensation curves was the same for all persons. A certain amount of evidence on this matter has been obtained by Abney by the study of the minimum intensity of light required for vision. For the present, however, we are confining ourselves to a study of the relative sensations produced by given amounts of light of different colours for each observer separately. Thus we take some one kind of light as a standard and compare the relative stimulation of the sensations produced by other kinds of light with that produced by this standard light. This is what is done when determining a luminosity curve, the particular light chosen as a standard being white light, *i.e.* the light which we are going to use to produce the spectrum which supplies the different colours which are to be used in the measurements.

Having to use white light as a standard, when we come to compare the measures made by a person having defective colour vision with those made by a normal, the matter is complicated by the fact that the unit with which the comparison is made, that is the white, is not the same for both. The defective sensation will not only affect the sensation received from the coloured light, but also that received from the white. Abney's theory as to the way the sensation curves of persons having defective colour vision differ

* Another way in which we might have a departure from the normal would be if, say, the green sensation curve were displaced in such a way that its maximum occurred at a different wave-length. There seems evidence that such a displacement may occasionally be met with, and the author hopes shortly to discuss this question in another communication. He has calculated the luminosity curves corresponding to such displacement and finds that they all intersect at neighbouring points, which do not coincide with the point P referred to on p. 411.

from the normal, however, enables us to get over this difficulty, as will be shown below.

As long as we confine our attention to the part of the spectrum between the extreme red and the blue, the effect of the blue sensation on the luminosity may in general be neglected as being too small to produce any appreciable effect*; hence, in what follows, the effect of the red and green sensations on the luminosity will alone be considered.

The easiest way to show the manner in which the luminosity curve of a colour-deficient person is obtained will be to consider a particular case, say, one where the red sensation is deficient to such an extent that all the ordinates of the red sensation curve are only half the normal. Such a person may be said to possess half-normal red sensation and will be indicated by the symbol 0·5 R.S. Since each of the ordinates of the red sensation curve is half the normal, the total area of that curve will also be half the normal. As in the light from the crater of the electric arc the areas of the red and green sensation curves are as 579 to 248, it follows that the areas for the 0·5 R.S. are as 290 to 248.

Now suppose such a person determines the luminosity of a colour of which the wave-length is λ, and that λ_r and λ_g are the ordinates of the normal red and green sensation curves for this colour, the corresponding ordinates for the observer will be $\frac{1}{2}\lambda_r$ and λ_g. The total sensation produced by the colour will be the sum of the two sensations, that is, for the normal it will be $\lambda_r+\lambda_g$ and for the observer (0·5 R.S.) $\frac{1}{2}\lambda_r+\lambda_g$.

The sensation produced by the comparison white in the luminosity measurement will be proportional to the sum of the areas of the red and green sensation curves. Hence, if we represent the areas of these curves for the normal by Σr and Σg respectively, the sensations produced by the white for the normal will be $\Sigma r+\Sigma g$, and for the colour-deficient will be $\frac{1}{2}\Sigma r+\Sigma g$.

Thus the brightness of the coloured light is for the 0·5 R.S. observer reduced in the ratio $(\frac{1}{2}\lambda_r+\lambda_g)/(\lambda_r+\lambda_g)$, while that of the white is reduced in the ratio $(\frac{1}{2}\Sigma r+\Sigma g)/(\Sigma r+\Sigma g)$. Let w be the intensity of the white when the normal observer makes the luminosity setting and w' the intensity of the white when the colour-deficient observer makes the setting. Then we have

$$w = a\,\{\lambda_r+\lambda_g\} \tag{1}$$

and

$$w'\frac{\{\frac{1}{2}\Sigma r+\Sigma g\}}{\Sigma r+\Sigma g} = a\,\{\tfrac{1}{2}\lambda_r+\lambda_g\}, \tag{2}$$

where a is a constant which depends on the unit used to measure the intensity of the white light.

* In the case of a normal eye the total luminosity due to the blue sensation when white light enters the eye is only about 1/200 of that due to the red sensation.

Thus the ratio of the colour-deficient observer's luminosity to that of the normal is given by

$$\frac{w'}{w} = \frac{\frac{1}{2}\lambda_r + \lambda_g}{\lambda_r + \lambda_g} \times \frac{\Sigma r + \Sigma g}{\frac{1}{2}\Sigma r + \Sigma g}. \tag{3}$$

Thus, knowing w, we can calculate what is the ordinate w' of the luminosity curve for the 0·5 R.S. observer corresponding to the colour λ.

The following statement may make the above argument clearer. When a colour-deficient observer makes a luminosity setting he matches the brightness of the colour as it appears to him against the brightness of the white as this appears to him. Owing to his deficiency both the colour and the white appear less bright. If there were no reduction in the brightness of the white to him, his luminosity setting would be $(\frac{1}{2}\lambda_r + \lambda_g)/(\lambda_r + \lambda_g)$ of the normal setting. Owing, however, to the comparison white being also reduced in brightness the size of his white unit is reduced in the ratio of $\frac{1}{2}\Sigma r + \Sigma g$ to $\Sigma r + \Sigma g$; and hence, as the size of the unit has decreased, he requires more of these units to match the colour, that is, we must multiply the number given above by $(\Sigma r + \Sigma g)/(\frac{1}{2}\Sigma r + \Sigma g)$. This decrease in the value of the white unit is the reason why the luminosity curve for a red-blind observer is higher than the normal in the green, and that for a green-blind observer it is higher than the normal in the red. These high values do not indicate that a red-blind person receives a greater stimulus from a given green light, or a green-blind receives a greater stimulus from a red light, than does a normal, but simply that relatively to the stimulus received from a given white light the stimulus received is greater.

Using equation (3) and the luminosity curves for a normal eye given by Abney, the luminosity curves for persons having the following red sensations in terms of the normal, namely, 0 R.S., 0·33 R.S., 0·7 R.S., and the following green sensations 0 G.S., 0·33 G.S., and 0·6 G.S., have been calculated. The results together with the normal luminosity curve are shown in fig. 2.

It will be observed that all the luminosity curves intersect at one point, P, which corresponds to S.S.N. 48·8 or a wave-length 5770 Å.U. The condition that the luminosity should be the same for the normal as for, say, the 0·5 R.S. observer is that [equations (1) and (2)]

$$\{\tfrac{1}{2}\lambda_r + \lambda_g\} \frac{\Sigma r + \Sigma g}{\frac{1}{2}\Sigma r + \Sigma g} = \lambda_r + \lambda_g,$$

or

$$\frac{\lambda_r \Sigma g}{2} = \frac{\lambda_g \Sigma r}{2}, \quad \text{or} \quad \frac{\lambda_r}{\lambda_g} = \frac{\Sigma r}{\Sigma g}, \tag{4}$$

that is at a wave-length such that for both observers the ratio of the ordinates of their red and green sensation curves is the same as the ratio of

the total areas of these curves.* Equation (4) shows that the wave-length of the light corresponding to the point of intersection is independent of the amount or kind of the deficiency in colour sensation of the observer.

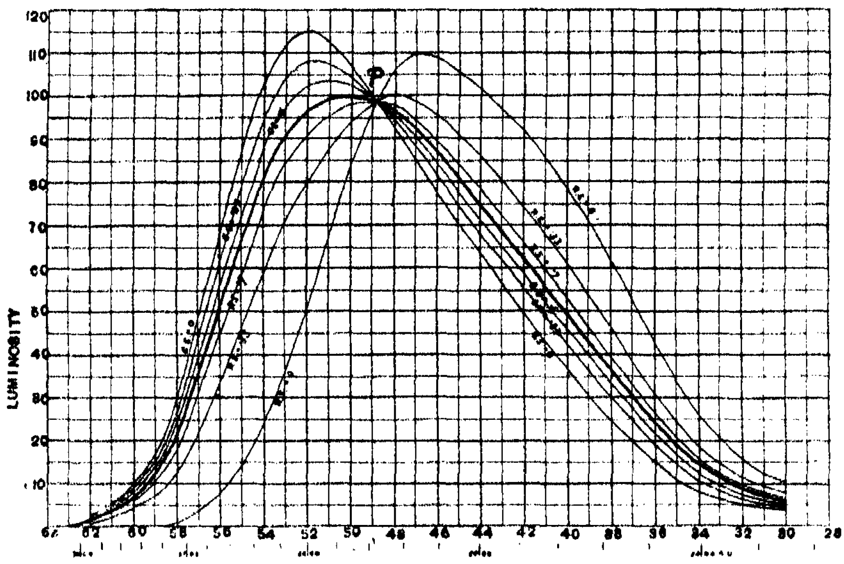


FIG. 2.

The curves given in fig. 2 depend on—

(1) The accuracy of Abney's sensation curves.

(2) The correctness of Abney's theory that in the case of the ordinary types of total or partial red or green colour-blindness the ordinates of one of the sensation curves are all reduced in the same proportion, and

(3) The additive property which has been assumed and which involves the corollary that the areas of the luminosity curves obtained by normal and colour-deficient persons are the same. Thus if it can be shown that the observed luminosity curves of persons who are colour deficient agree with the calculated curves it is strong evidence in favour of the correctness of the above three assumptions.

To test this point the observed luminosities obtained by colour-deficient observers will be shown plotted on diagrams containing the calculated curves shown in fig. 2, so that it will be possible to see at a glance whether (1) the observed points all lie on one of these curves or lie uniformly between two adjacent curves indicating that the observer belongs to a class intermediate

* The wave-length at which all the curves will intersect depends on the distribution of light in the spectrum employed in the experiments, *i.e.* on the source of light.

between those for which the curves are plotted, and (2) whether the luminosity is the same for all for one particular colour.

Two sets of data will be used to test the validity of the calculated curves. In the first place Sir William Abney has published in various papers the results of a large number of measurements of luminosity for colour-deficient persons. These measurements extend over many years and the numbers given do not always directly enable us to test the question, since the scales on which they are given vary; in many cases the maximum luminosity for each observer is taken as 100, but other scales for the ordinates are also employed. However, by making use of the fact that if the curves were all plotted on the same scale then the areas must all be the same (the source of light and the spectroscope were the same throughout), the factors by which the values given must be multiplied so as to make the areas equal have been calculated. When these factors have been applied the curves will all be on the same scale. In each individual case the same factor of course is used for all the observations. The readings reduced in this manner to the same scale are those given in the figures. These data make a peculiarly valuable test because the numbers used were all published before the calculated curves, which we are going to use them to test, were obtained and in fact some of them were published* before the sensation curves used in the calculations had been obtained. It is also open to anyone to check the results by reference to the original papers.

Secondly, use is made of a selection from a large number of fresh measurements obtained in a different manner. Since the equality of brightness method of obtaining the luminosity curves described above, involving as it does the comparison of the brightness of two lights which differ greatly in colour, is a process which requires considerable practice, although given such practice Abney's numbers show that concordant measures can be obtained, the flicker method originally described by Ferry,† has been utilised for the determination of luminosity curves. In one arrangement which has been found to give good results, even with quite inexperienced observers, a cylinder of large diameter rotating about a horizontal axis is placed between the movable slit and the screen on which the light is received. Segments are cut out of the circumference of the cylinder so that the screen is alternately illuminated by the coloured light and the comparison white, both kinds of light falling on the same part of the screen. In order to obtain satisfactory measurements it is essential that the alternations from colour to

* Sir W. Abney has stated in one of his papers that the numbers given in the papers which are quoted were all obtained before he had determined the sensation curves.

† 'Amer. Journ. Sci.,' 1892, vol. 44, p. 192.

white and *vice versâ* should take place without overlap or gap between the lights. If either of these occur then complete absence of flicker can only be obtained when the speed of flicker is high, and under these conditions the sensitiveness of the method is too low to admit of satisfactory measurements being obtained.

Since with a flicker method it is impossible to alter the intensity of the white by means of rotating sectors, for if this is done a phenomenon analogous to beats is obtained, use was made of an annulus of gradually increasing density placed in the white beam. This annulus had been calibrated by Sir William Abney, and is described in one of his papers.*

Another form of flicker apparatus† has also been used, in which the source of light is a Nernst filament and in which the alternations are caused by rotating a disc between the filament and the collimator lens. Half of the circumference of this disc is cut away and the other half forms a mirror from which the white light used for the comparison light is reflected. Thus, during half the time of rotation of the disc the light passes through to the spectroscope, and during the other half it is reflected to form the comparison light. In this instrument the intensity of the white light is altered by altering the relative positions of two systems of lenses which are placed in the path of the white light.

In the flicker experiments the light was received on a block of compressed magnesium carbonate, of which the surface had the form of a square, each edge being 18 mm. This surface was at a distance of 60 cm. from the eye, so that each side of the square subtended an angle of 1° 43′ at the observer's eye.

The luminosity curves obtained by the flicker method differ slightly from those obtained by the equality of brightness method, particularly in the green and blue. These differences have been the subject of a separate investigation carried on by Sir W. Abney and the author, and they hope to be able to communicate the results shortly.

Since, at any rate to a first approximation, the additive law applies to flicker measurements,‡ without considering the differences between the luminosity curves obtained by the two methods, we may by a similar line of reasoning to that used above calculate from the normal flicker luminosity curve the flicker luminosity curves for the colour-deficient, and then by

* 'Phil. Trans.,' 1897, A, vol. 190, p. 156.

† The cost of which has been partly defrayed by a grant from the Government Grant Committee.

‡ Tufts, 'Physical Review,' 1907, vol. 25, p. 438; Whitman, 'Physical Review,' 1896, vol. 3, p. 248.

comparing these calculated curves with the observed curves we can test the accuracy of the calculated curves and consequently the correctness of the assumptions on which they are based.

§ 3. Taking first the measurements previously published, the observed points are shown plotted in figs. 3 to 7. To save space the points corresponding to two observers are plotted on the same figure, while the references to the paper in which the original measurements are published are given below each figure.*

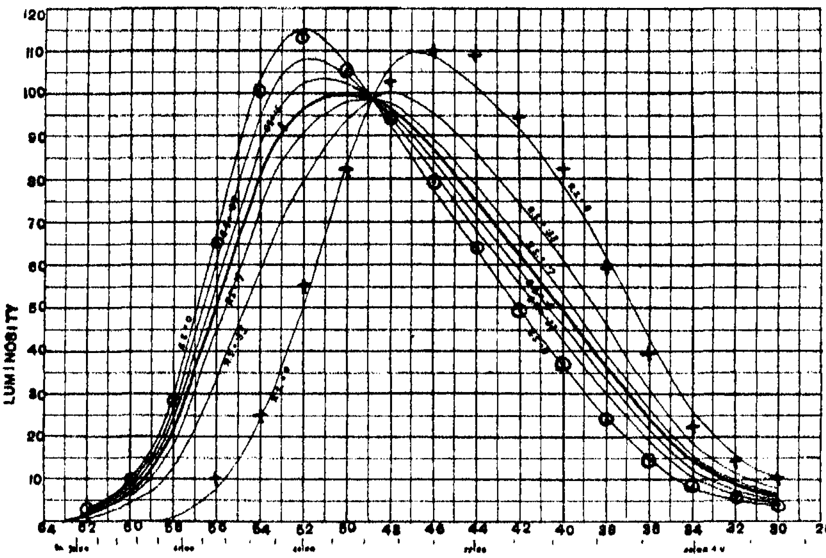


FIG. 3.

+ L. } 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 472.
⊙ F. }

In figs. 3 and 4 we have examples of persons who have R.S. = 0 and G.S. = 0 respectively. In fig. 5 observer D has G.S. = 0 and observer Z has R.S. = 0·33. In figs. 6 and 7 we have two examples of persons having R.S. = 0 and one having G.S. = 0·2.†

It will be noticed that when the observed points are plotted on such a scale that the area of the curve drawn through them is the same as the

* All the numbers given in this paper were obtained when the observer was dark adapted.

† On plotting the numbers given in the 'Philosophical Transactions' for V. H., it was obvious that some error had crept in, and on submitting the matter to Sir W. Abney, he said he had already noticed that, owing to a mistake when reducing the scale readings of the instrument to S.S.N., the numbers as given were erroneous. He has kindly looked up the original measurements and the points given in fig. 6 are obtained from these numbers.

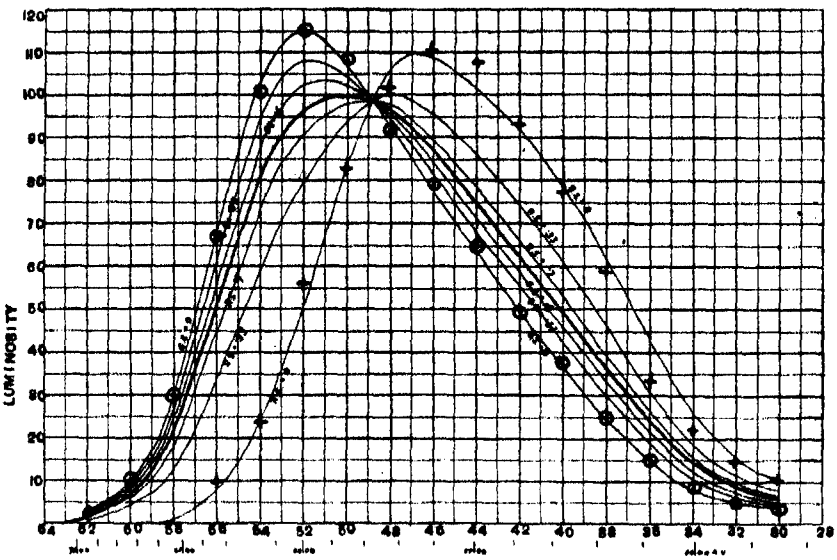


FIG. 4.

+ H.
⊙ E. } 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 472.

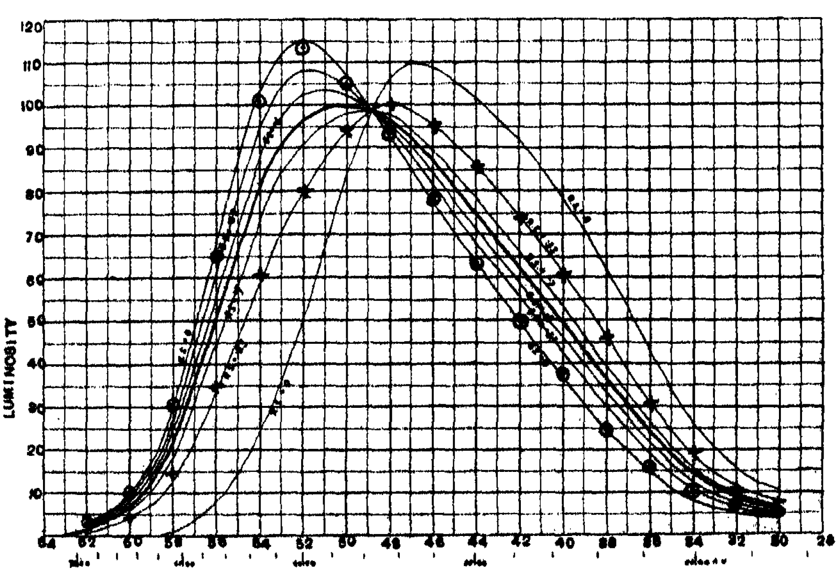


FIG. 5.

+ Z., 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 460.

⊙ D., 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 472.

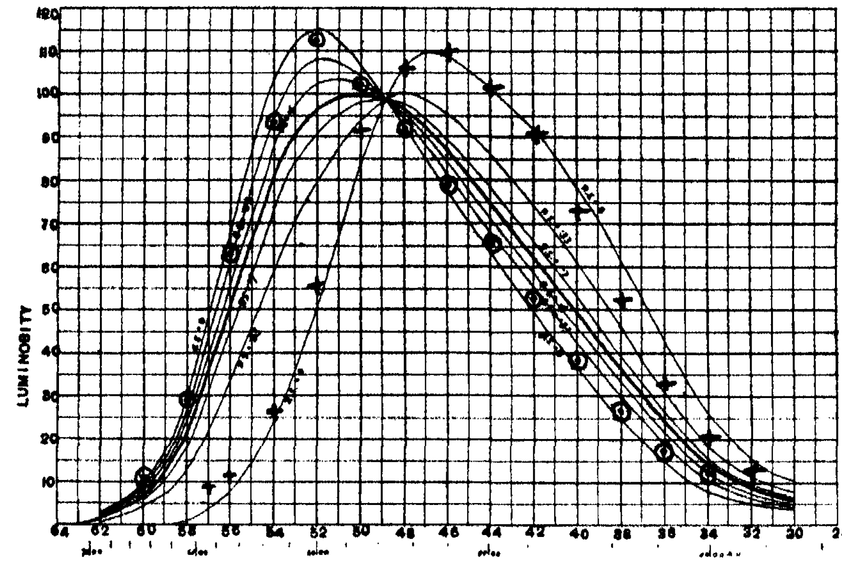


Fig. 6.

\+ H. R., 'Phil. Trans.,' 1892, p. 556.

⊙ V. H., 'Phil. Trans.,' 1892, p. 555.

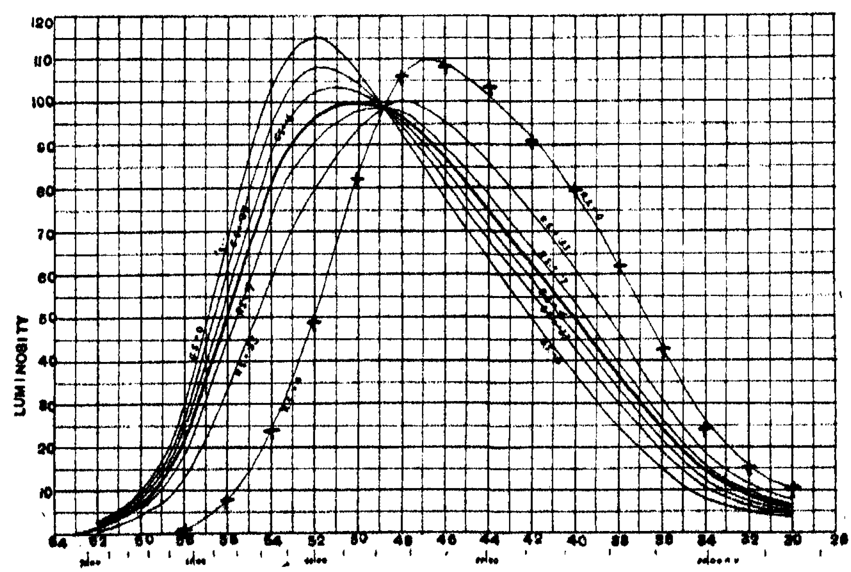


Fig. 7.

\+ X., 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 466.

area of the normal curve, all the luminosity curves intersect at a single point, that is, for this particular point of the spectrum the luminosity is the same for all. Further, the plotted points agree quite well with the calculated curves. Any departure which is found is mostly confined to the greenish-blue, where, as has been already mentioned, differences may be expected, since, in the first place, when obtaining the calculated curves, we have neglected the effect of the blue sensation, and further (as will be shown in § 5), slight differences in macular pigmentation begin to be important in this region.

§ 4. A few examples of the results obtained by the flicker method are given in figs. 8, 9, and 10. The normal curve* is shown in each figure by the thick line. It will be observed that the normal curve differs from that obtained by the equality of brightness method given in fig. 2. This difference is partly due to a difference in the source of light employed. The flicker

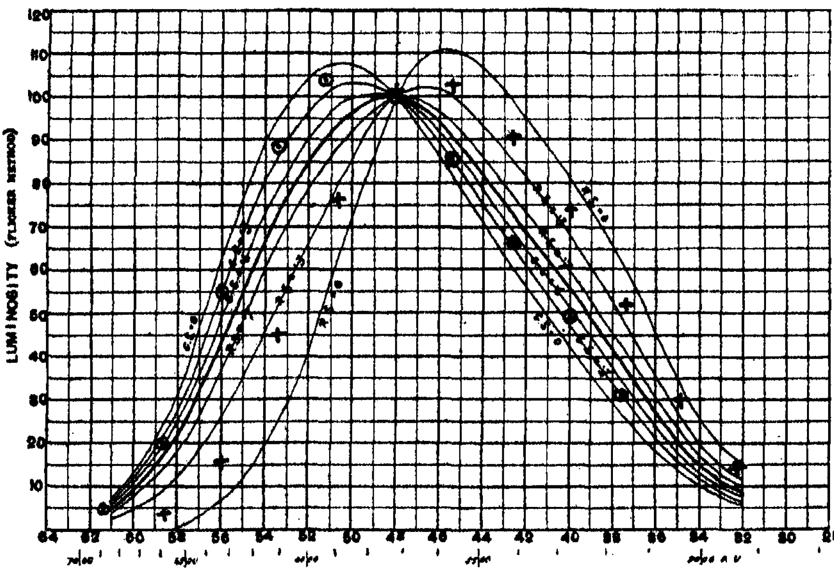


FIG. 8.
+ No. 1. ⊙ No. 2.

curves were obtained with an arc in which the positive carbon was horizontal, so that the crater is directly facing the slit of the spectroscope. The equality of brightness curves were obtained using an arc with nearly vertical carbons, so that the crater was turned more or less edgeways towards the slit. Most of the difference between the two curves is, however, a real difference, due to the difference of method. This difference is most marked in the green and

* *May* 5, 1913.—This is the mean obtained by 10 observers.

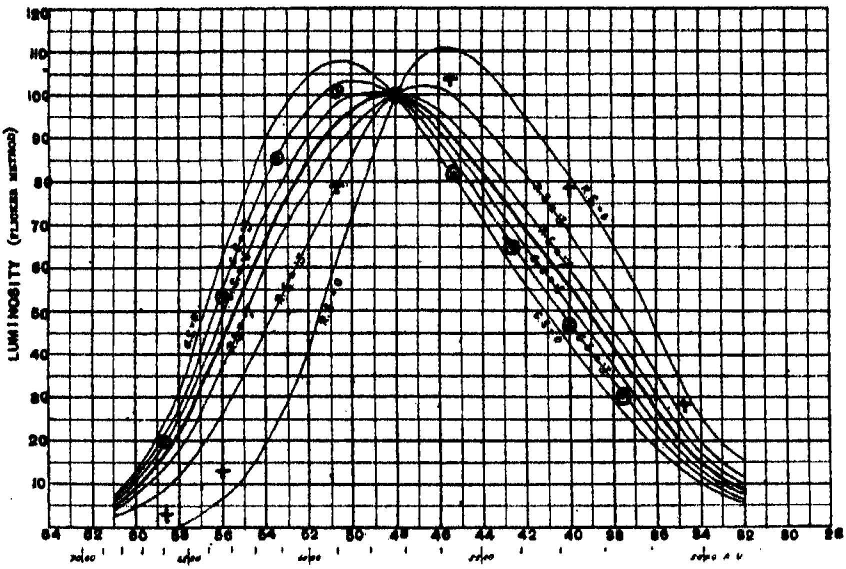


FIG. 9.

+ No. 4. ⊙ No. 3.

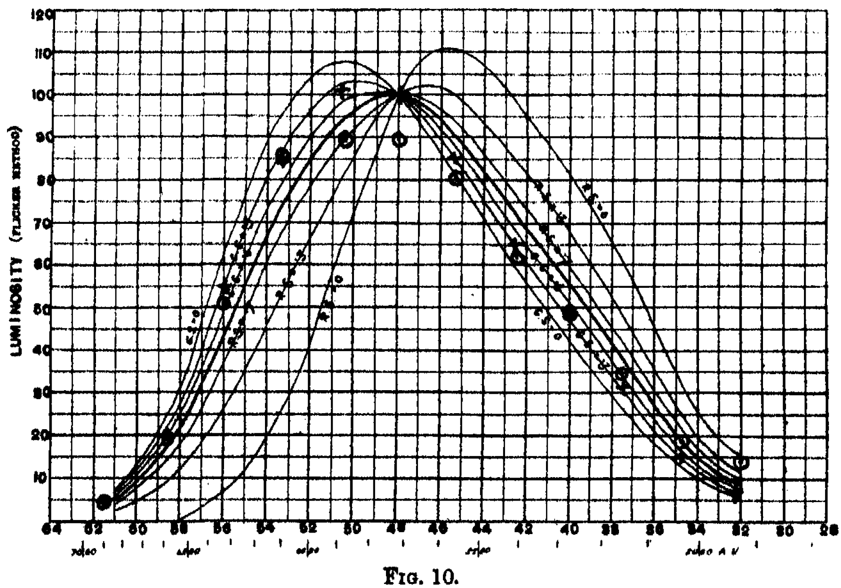


FIG. 10.

+ No. 5, foveal. ⊙ No. 5, parafoveal.

blue, and has been examined by Ives* in a series of most interesting and valuable papers. When comparing the results given in this paper with those given by Ives, it must be noted that Ives, in place of varying the intensity of the comparison white, varies the intensity of the coloured light. Hence, in his experiments, the brightness of all parts of the spectrum was equal when the comparisons with white were made, while, in my experiments, the brightness of the coloured light, and hence also of the comparison white, was very much less at the ends of the spectrum than at the middle.

In fig. 8, Observer 1 has about 0·2 R.S., while Observer 2 has about 0·3 G.S. In fig. 9, Observer 4 has about 0·2 R.S., and Observer 3, 0·3 G.S. In fig. 10, the points marked by a + show that Observer 5 has a little over 0·3 G.S.

Observer 1 has a shortened spectrum, a neutral point, and he mistakes red for green, and *vice versâ*. He matches a mixture of green and violet light with white, and any amount of deep red light could be added to the mixture without his being aware that any change had been made, although this addition of red caused the mixture, to a normal eye, to change from a bluish-green to a bright red. He is quite unable to correctly distinguish the colours of ships' lights.

Observer 2 has a neutral point, and calls the green of this part of the spectrum white. He often calls a green light white or a white light green, and, with lights of small intensity and small angular magnitude, he occasionally confuses green and red.

Observer 3 frequently calls white green and green white, and, with lights of small angular magnitude, he occasionally calls red green.

Observer 4 has a shortened spectrum and confuses red and green. With ships' lights, at distances up to 2 sea miles, he made over 20 per cent. of mistakes.

Observer 5 has a neutral point and calls green white and white green. If a little white light is added to any green, he calls the mixture white, although to a normal eye it still appears a fairly saturated green.

§ 5. In the preceding two sections examples have been given of what may be termed "normal" luminosity curves for persons having both normal and defective colour vision. The great majority of the luminosity curves obtained belong to this class. In a few cases, however, both of persons possessing normal colour vision and of those possessing defective colour vision, the luminosity curves differ in that they do not agree with any of the curves given in fig. 2, nor do they lie uniformly between any adjacent pair.

Taking first the case of abnormal curves given by persons who have normal colour vision. In figs. 11 and 12, the points marked by +, and through

* 'Phil. Mag.,' July, September, and December, 1912.

which the chain-dotted line is drawn, correspond to the luminosity measurements made by two such observers. In neither case do the curves pass through the point P, one curve passing considerably above this point and the

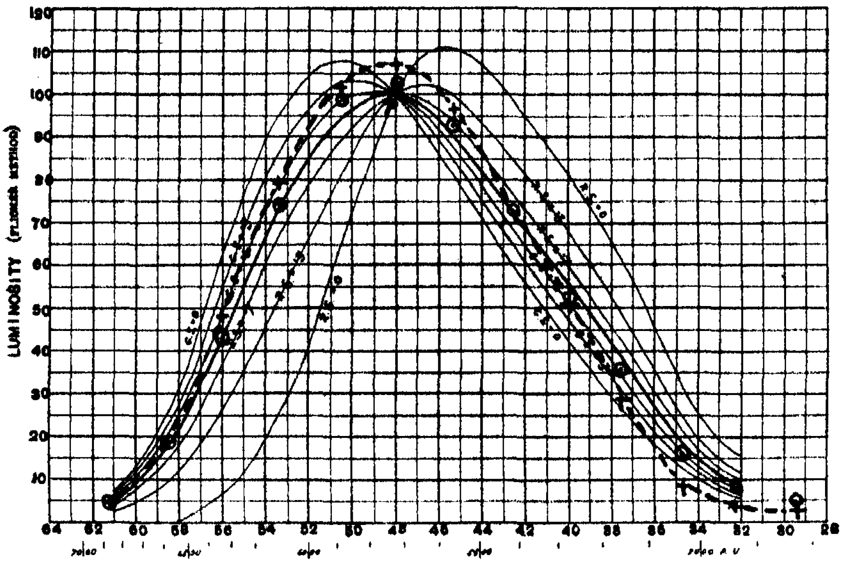


FIG. 11.
+ No. 6, foveal. ⊙ No. 6, parafoveal.

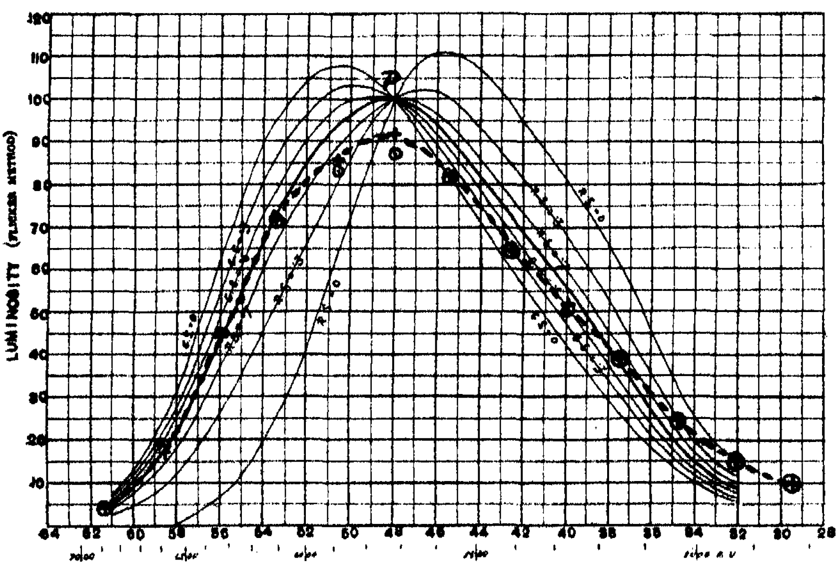


FIG. 12.
+ No. 7, foveal. ⊙ No. 7, parafoveal.

other below. The difference from the normal seems to be due to a cause to which Maxwell* called attention, namely, the pigmentation of the yellow spot. Thus it would appear that Observer 6 has more pigmentation at the fovea than the normal, and Observer 7 has less. In order to test the correctness of the above explanation, the luminosity curves of these observers, as well as of the author, were obtained when the image formed on the retina was confined to a region surrounding the fovea, that is to what, for short, may be called the "parafoveal" region. For this purpose the surface on which the colour and the white were received alternately had the form shown in fig. 13. It consisted of a white ring of which the diameter of the internal

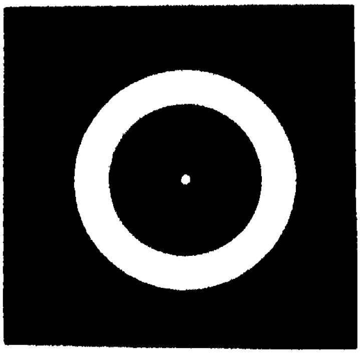


FIG. 13.

border subtended an angle of 3° 22′ at the eye of the observer, while the external border subtended an angle of 5°. A small white dot at the centre served to fixate the eye. Although this arrangement is more difficult to use than the small square, yet with a little practice fairly good settings could be obtained. The points marked ⊙ in figs. 11, 12, and 14 give the results obtained for the parafoveal region for Observers 6, 7, and the author.

The first thing that strikes one is that in the case of Observer 7 the luminosity curve is practically the same for the parafoveal and the foveal regions, and that both of these agree with the author's parafoveal curve. Next, in the case of Observer 6, the parafoveal curve more nearly agrees with the foveal curve for the normal. This distinction is brought out very clearly in fig. 15, where the ratio of the parafoveal luminosity to the foveal for No. 7 and W. W. are shown. It will be seen that for Observer 7 the ratio is practically constant and equal to unity throughout the spectrum, while for W. W. the ratio increases rapidly as the blue end of the spectrum is reached. It would thus appear that Observer 7 has no more pigment at

* 'Phil. Trans.,' 1860, vol. 150, p. 76.

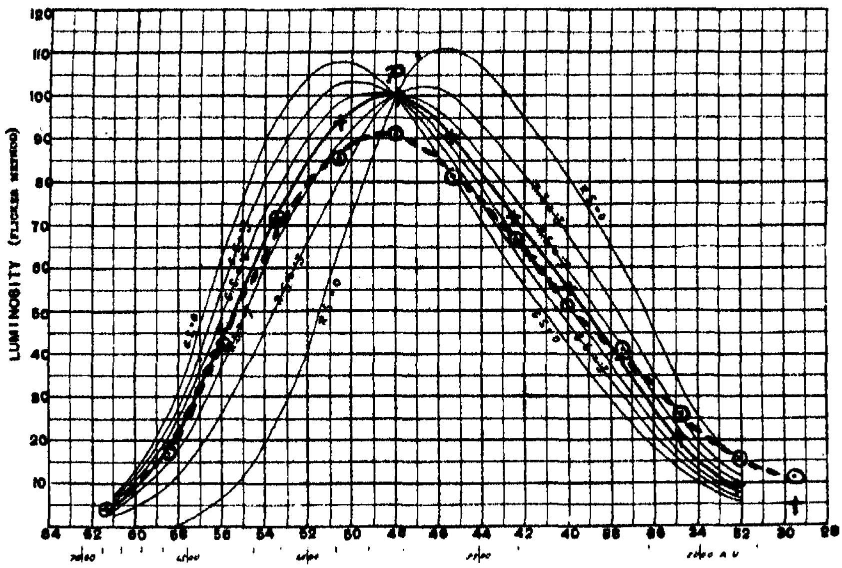


FIG. 14.

+ W. W., foveal. ⊙ W. W., parafoveal.

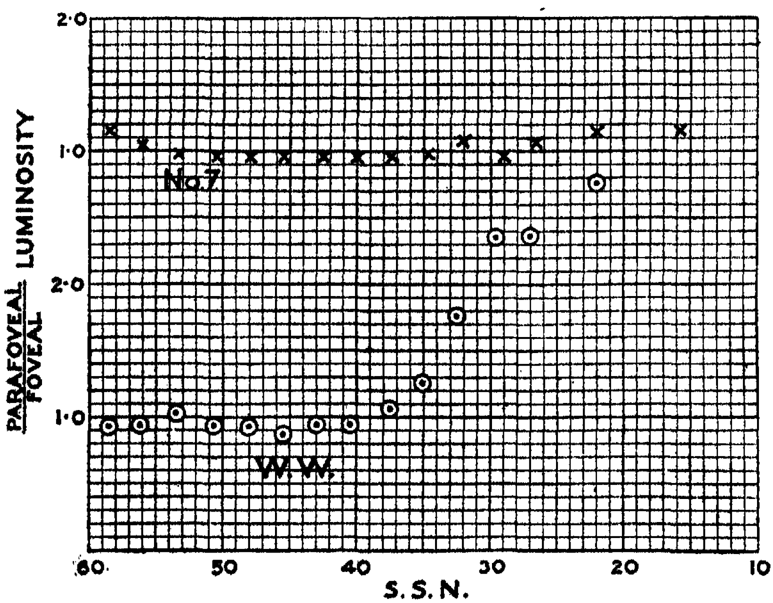


FIG. 15.

his fovea than the normal possesses in the parafoveal region. Further, the results support the view that Observer 6 has more than the normal amount of pigmentation at his fovea and also in the parafoveal regions. When Observer 7 made his settings, using spectacles fitted with light canary-coloured glass, his luminosity curve for foveal vision agreed almost exactly with the normal curve. In the case of Observer 7 the absence of the yellow pigment, which to the normal eye produces marked absorption in the blue and violet regions of the spectrum, enabled him to make accurate flicker settings far down into the violet, where to the normal eye the light is too feeble to allow of good settings being obtained. On the other hand Observer 6 cannot make reliable settings beyond the blue-green, the light appearing to him too feeble.

Observer 6 appears to have quite normal colour sense, although when matching a white by means of a mixture of red, green, and violet light he requires little or no violet, the reason being that owing to macular absorption the white is to him much "yellower" than to a normal eye, and hence the mixture of red and green which to the normal looks yellower than the white appears to him a correct match. He is quite good at matching blues and violets.

Observer 7 has also normal colour sense, although for his white match he uses more violet than the normal.

In figs. 16 and 17 are shown the flicker luminosity curves of two observers who have defective colour vision, the green sensation being in each case in defect, and who, in addition, appear to have more than the normal amount of pigmentation of the fovea. In fig. 18 Observer M* has more pigmentation than the normal, and his G.S. is practically zero. Observer N. W., on the other hand, is defective as to red sensation but has less pigmentation than the normal. It would be very interesting to examine the parafoveal luminosity curves for these colour-deficient observers, but unfortunately up to now it has been impossible to get them to devote the necessary time to make the observations.† The parafoveal curve for Observer 5 is indicated by the points marked ⊙ in fig. 10. The pigmentation of this observer appears to be normal.

In fig. 19 are given the luminosity curves of two persons who were

* The values given in figs. 18, 19, 20 were all obtained by the equality of brightness method.

† A displacement of the green sensation curve towards the red end of the spectrum would give a luminosity curve very like those obtained by Observers 8 and 9. A study of their parafoveal luminosity curves might enable one to say whether they are cases of green deficiency plus abnormal macular pigmentation or cases of such displacement.

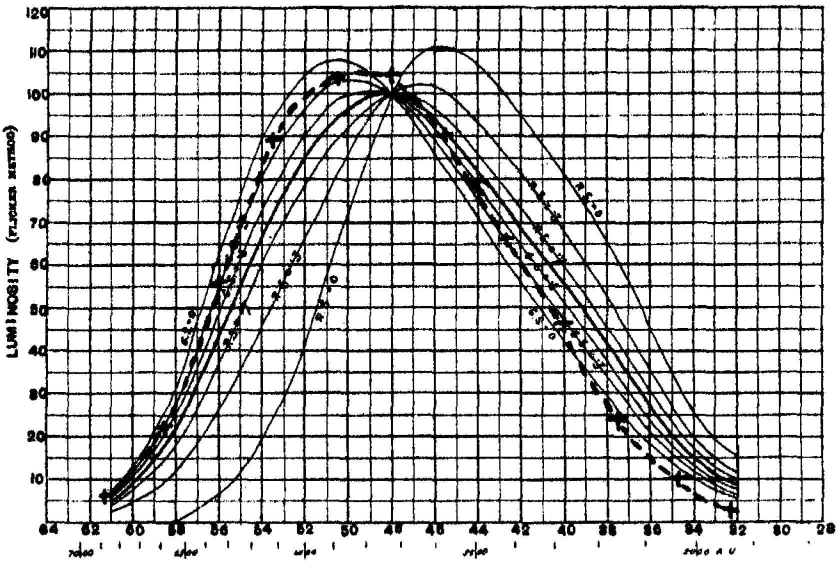


FIG. 16.
+ No. 8, foveal.

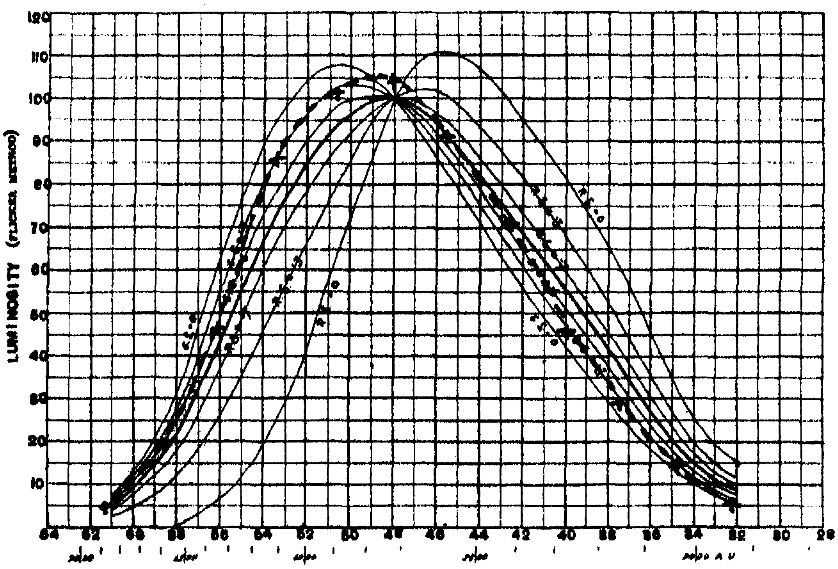


FIG. 17.
+ No. 9, foveal.

suffering from tobacco scotoma, and it will be observed that the curves are of an entirely different type to any of those previously given. In fig. 20

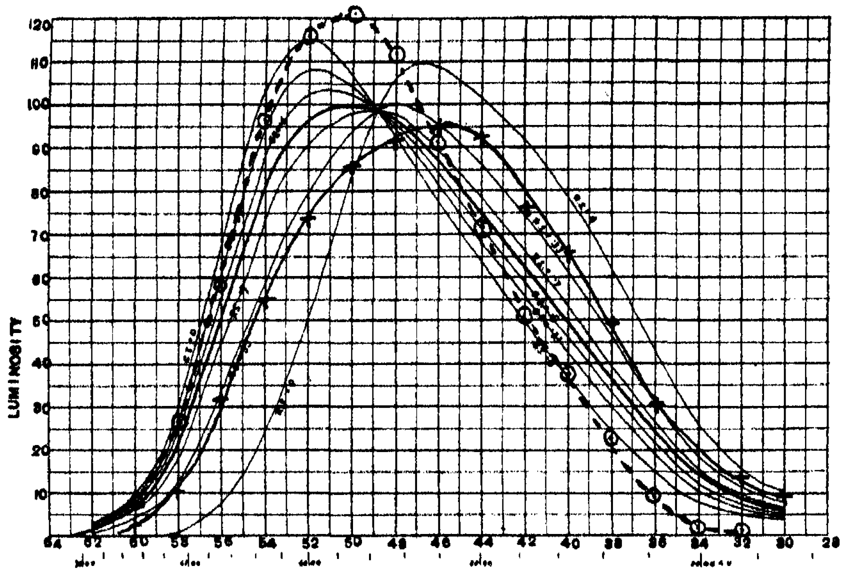


FIG. 18.

+ N. W. 'Roy. Soc. Proc.,' 1891, vol. 49, p. 503.

⊙ M., 'Phil. Trans.,' 1892, A, vol. 183, p. 551.

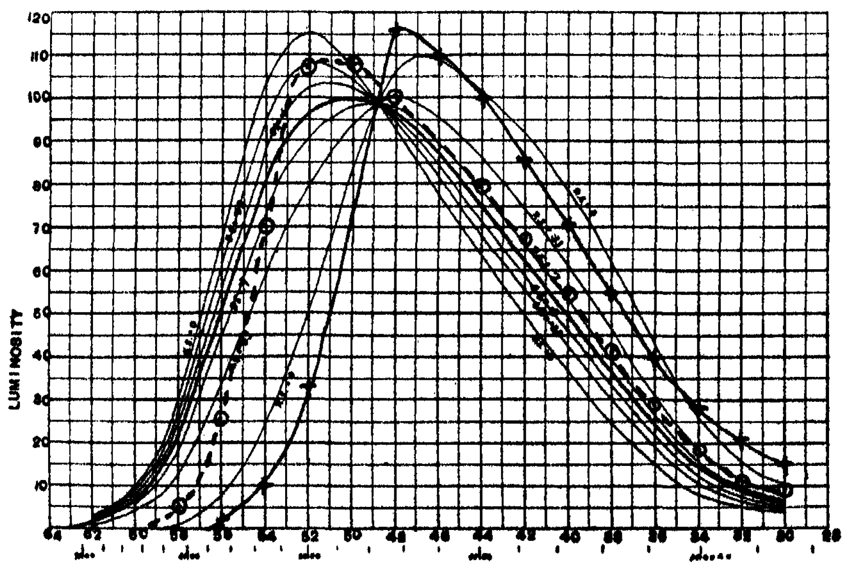


FIG. 19.

+ G., 'Roy. Soc. Proc.,' 1891, vol. 49, p. 502.

⊙ C., 'Roy. Soc. Proc.,' 1891, vol. 49, p. 493.

are given the curves for two observers who are colour blind, the defect being due to disease (atrophy of the optic nerve). In one case (Miss W.)* the curve very nearly agrees with the normal, while in the other the curve somewhat resembles that of Observer 7. It would thus appear that in the case of disease the colour-blindness which is produced is of an entirely different type to that which is found in cases of congenital colour-blindness. If this is the case comparison of the luminosity curves of the two classes of colour-blinds seems as if it might give us valuable information as to the seat of the colour-perceiving apparatus.

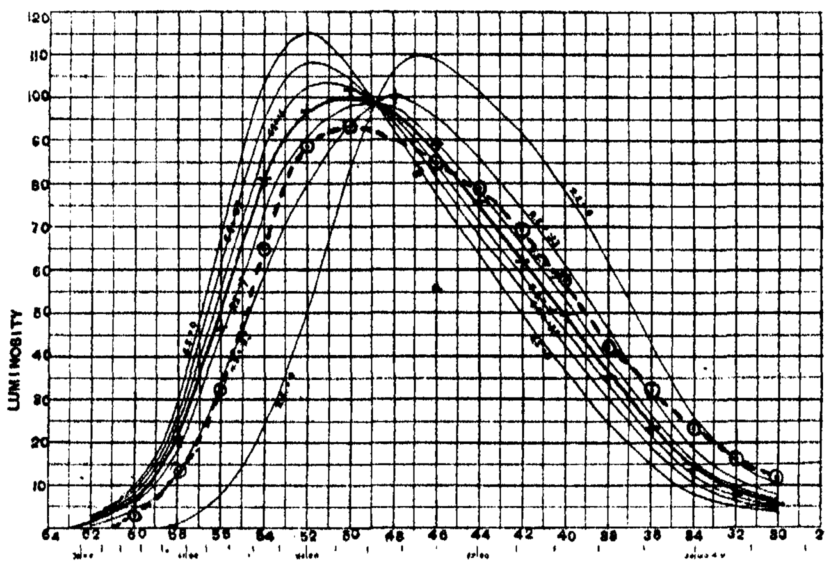


Fig. 20.
+ Miss W., 'Roy. Soc. Proc.,' 1891, vol. 49, p. 507.
⊙ W. S., 'Roy. Soc. Proc.,' 1891, vol. 49, p. 498.

The examples of the luminosity curves of different colour-deficient persons which have been given form only a small proportion of the cases which the author has examined. They will, however, be sufficient to show that the assumptions on which the calculated curves are based must, in the main, be true. Abney's theory that the different classes of the more commonly occurring forms of congenital colour defect are due to different degrees of deficiency in the red or green sensations is so strongly supported as to practically amount to a complete proof. It must be remembered that the

* The eye tested had become "colour blind" after a stroke of paralysis; the other eye was still normal.

investigation given above has been confined to that portion of the spectrum on the red side of the blue. If we wish to extend our investigation into the blue and violet then we should have to take account of the effect of the blue sensation. Further, although it seems quite clear that the major part of the luminosity perceived in that part of the spectrum including the red, yellow and green, at any rate with fairly bright spectra, is due to the red and green sensations, there is much evidence to indicate that, at any rate in the green and blue, there is a fourth sensation which may be called the fundamental white sensation. This probably corresponds to the rod-effect of von Kries, which would have to be taken into account if extremely minute differences of luminosity were under consideration, or if we were dealing with spectra of small intensity.

The Reflection of X-rays by Crystals.

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the University of Leeds; and W. L. Bragg, B.A., Trinity College, Cambridge.

(Received April 7,—Read April 17, 1913.)

In a discussion of the Laue photographs it has been shown* that they may conveniently be interpreted as due to the reflection of X-rays in such planes within the crystal as are rich in atoms. This leads at once to the attempt to use cleavage planes as mirrors, and it has been found that mica gives a reflected pencil from its cleavage plane strong enough to make a visible impression on a photographic plate in a few minutes' exposure. It has also been observed that the reflected pencil can be detected by the ionisation method.†

For the purpose of examining more closely the reflection of X-rays in this manner we have used an apparatus resembling a spectrometer in form, an ionisation chamber taking the place of the telescope. The collimator is replaced by a lead block pierced by a hole which can be stopped down to slits of various widths. The revolving table in the centre carries the crystal. The ionisation chamber is tubular, 15 cm. long and 5 cm. in diameter. It can be rotated about the axis of the instrument, to which its own axis is perpendicular. It is filled with sulphur dioxide in order to increase the ionisation current: both air and methyl iodide have also been used occasionally to make sure that no special characteristics of the gas in

* W. L. Bragg, 'Proc. Camb. Phil. Soc.,' vol. 17, Part I, p. 43.

† W. H. Bragg, 'Nature,' Jan. 23, 1913.

the chamber affect the interpretation of the results. The ionisation current is measured directly. A balance method has not been used as we have not found it possible to deflect a suitable portion of the primary rays into a balance chamber.

The face of the box containing the X-ray bulb is covered with a special shield of lead, 5·5 mm. thick; the general lead covering of the box is 1 mm. thick, which is not always enough to screen the chamber from penetrating X-rays that produce an effect comparable with the effect of the reflected rays. The circular end of the ionisation chamber is also protected by lead. The slit through which the primary pencil of X-rays emerges from the box is 3·3 mm. long; its width has been 2 mm. for the rougher measurements and 0·75 mm. for the finer. Since the slit is 12 cm. from the anticathode the emerging pencil has an angular width of about a third of a degree in the latter case. In the same way a slit 2 mm. wide and 5 mm. long admits the reflected pencil to the ionisation chamber when preliminary measurements are being made, or when the whole effect is feeble; and this width can be cut down to 0·75 mm. when desired. The distance from either slit to the axis of the apparatus is 8 cm.

We have found it best to keep the bulb very "soft." The cathode stream has often been visible over its whole length.

As will be seen later it is desirable to determine angles of incidence and reflection with great accuracy. This was not anticipated, and the circular scale was only divided into degrees, and was made too small. Nevertheless, it is possible to read tenths of a degree; a better and more open scale is now being put in.

Let us suppose that a crystal is placed on the revolving table so that the cleavage face passes through the axis of the instrument. Let the incident pencil fall on the face and make an angle θ with it; and let the crystal be kept fixed while the ionisation chamber is revolved step by step through a series of angles including the double of θ, the ionisation current being measured at each step. The results of such a set of measurements are shown in fig. 1. In this case the crystal is rock-salt; and it has been placed so that the incident pencil makes an angle of 8·3°—as given by the apparatus—with the incident beam. The points marked in the figure show the result of setting the ionisation chamber at various angles and measuring the current in each case.

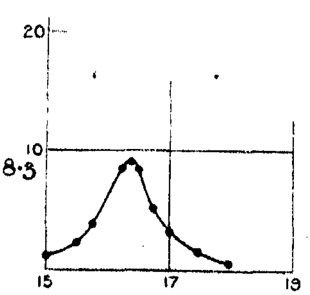


FIG. 1.—Regular reflection from cleavage face of rock-salt, glancing angle 8·3°.

The maximum effect is not quite at 16·6°, but at a point somewhat less than 16·4°. The defect from the double angle is due in part to want of symmetry and accuracy of the apparatus; but not much of it is caused in this way. It is rather due to the difficulty of setting the crystal face exactly; sometimes this is much accentuated by "steps" on the face of the crystal. The error can be eliminated by swinging over the ionisation chamber to the other side and taking corresponding observations, in a manner analogous to the method of finding the angle of a prism on the spectrometer.

The finer slits were used in obtaining this curve, and it may be inferred from the figure that the source of the X-rays is practically a point. For the width of the pencil from a point source by the time it reaches the slit of the ionisation chamber is $0·75 \times 28/12$ or 1·75 mm. The chamber slit being 0·75 mm. wide, the whole effect observed is comprised within a lateral movement of the chamber equal to $1·75 + 0·75$ or 2·50 mm. Since the chamber slit is 8 cm. from the axis of the apparatus this implies a rotation of the chamber through $(2·50 \times 180)/(\pi \times 80)$ or 1·78°. The figure shows that these limits are actually observed; the whole curve lies well within the range 15° to 18°. The source must therefore be nearly a point.

When the actual relation between the angles of the crystal mirror and the ionisation chamber has been determined, the mirror and chamber may be swept together through an extended range, keeping the relation between the angles such that the chamber always shows the maximum current for each setting of the crystal. It is convenient to use the wide slits for a preliminary examination of this kind. When the effect is small the wide slits can alone be used. But in a number of cases it is possible to use the narrow slits in order to make a closer survey, and where this is done much more information can be obtained.

The curve in fig. 2 shows the results of a sweeping movement of this kind, the crystal being iron pyrites. Curves for rock-salt are drawn in figs. 3, I, and 3, II. It will be observed that there are peculiar and considerable variations in the intensity of the reflection at different angles. The three peaks marked A, B, and C are common to the curves of all crystals so far investigated, *e.g.* zinc blende, potassium ferrocyanide, potassium bichromate, quartz, calcite, and sodium ammonium tartrate. They are readily distinguishable by their invariable form, relative magnitudes, and spacings. Moreover, the absorption coefficients of the rays reflected at these separate angles do not vary with the nature of the crystal or the state of the bulb. It happens that the actual angles of reflection of the three sets of rays are nearly the same for several crystals.

The use of the narrow slits permits a closer examination of these

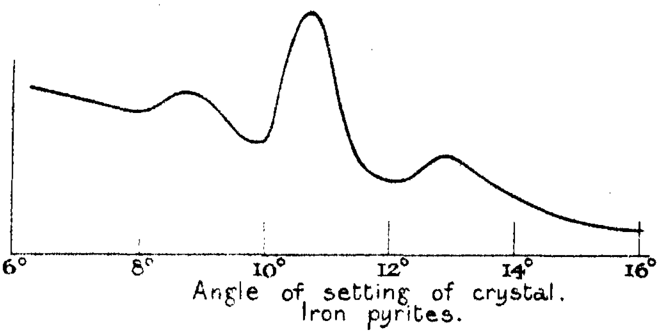


FIG. 2.—Reflection from face (100) of iron pyrites, at varying angles of incidence. Abscissa—Angle of incidence of rays on crystal face; Ordinate—Strength of reflected beam, arbitrary scale.

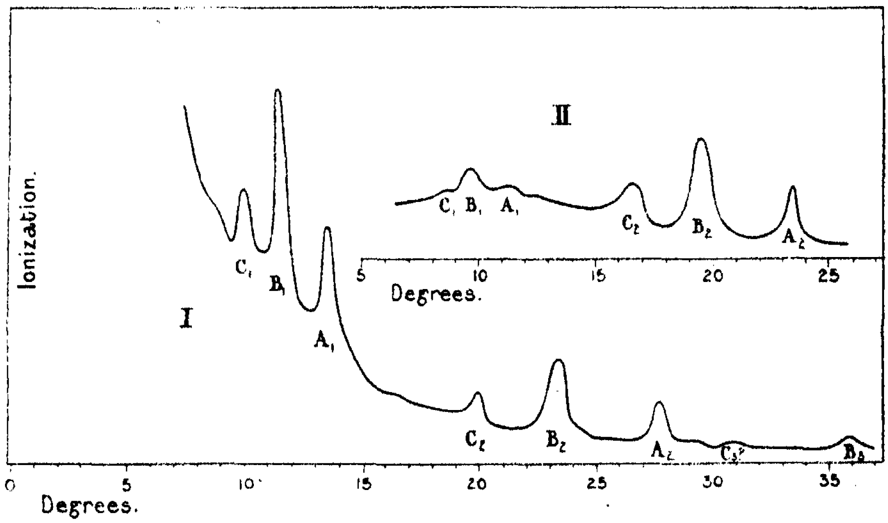


FIG. 3.—Reflection (I) from face (100) and (II) from face (111) of rock-salt. The curves show the variation of strength of reflected beam with angle of incidence.

effects; but, of course, it takes much longer time to make, and more space to exhibit. The results for iron pyrites are shown in the series of curves of fig. 4: a series in which each curve is obtained in the same way as the curve of fig. 1, the crystal being set at some definite angle which is altered in going from curve to curve. The curves are arranged so that the vertical distance between the horizontal lines of reference of any pair is proportional to the difference in the angles of setting of the crystal in the two cases.

In comparing the curves at the different angles two principles must be borne in mind. In the first place if there is a general reflection of rays throughout the whole range of the pencil which is emerging from the slit near the bulb, the curves show, as in fig. 1, a maximum with similar slopes

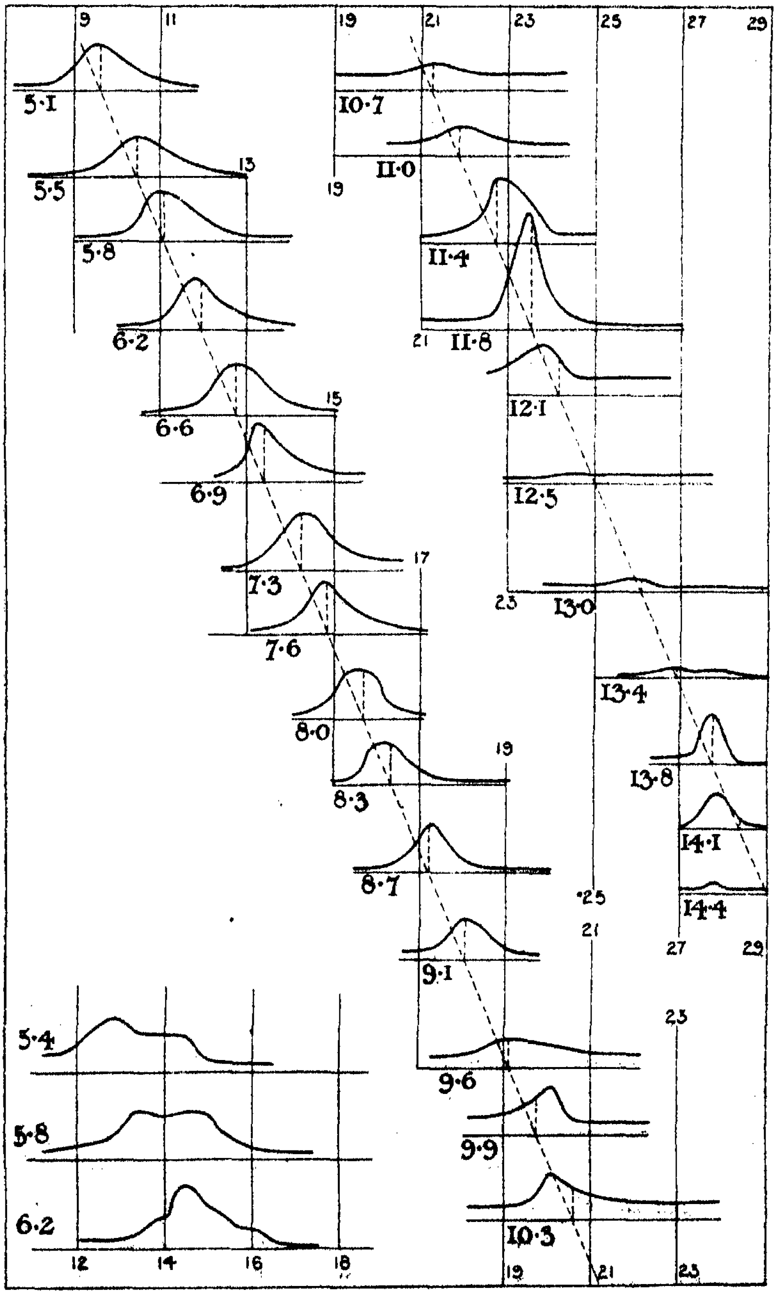


FIG. 4 (*a*). FIG. 4.

FIG. 4.—Detailed examination of reflection from iron pyrites (100).

on each side of it. The maximum occurs at that setting of the chamber which is twice the angle of setting of the crystal or differs from it only by that constant error of setting to which allusion has already been made. The maximum slowly marches across the page as we go down the series of curves, and its progress is marked by the dotted line.

In the second place there is a special reflection which manifests its presence in a curious and most convenient way. It often happens that the rays emerging from the bulb slit and falling on the crystal contain a large preponderance of rays of a given quality which can only be reflected at a certain angle. This angle is very sharply defined: even our present and somewhat rough apparatus shows that it is limited to a very few minutes of arc in either direction. In this case the radiation which is reflected is not distributed generally over the whole range bounded by the edges of the bulb slit, which it will be remembered is about a third of a degree, but is confined to a select small portion of that range. When this is the case the position of the maximum does not change at all as the crystal is moved from setting to setting, so long as any of this radiation is reflected. For example, the curves for 13·4°, 13·8°, 14·1°, 14·4° show the existence of a special reflection of this kind which is always at its maximum when the chamber is set at 27·7°. The reason for this may be understood from fig. 5.

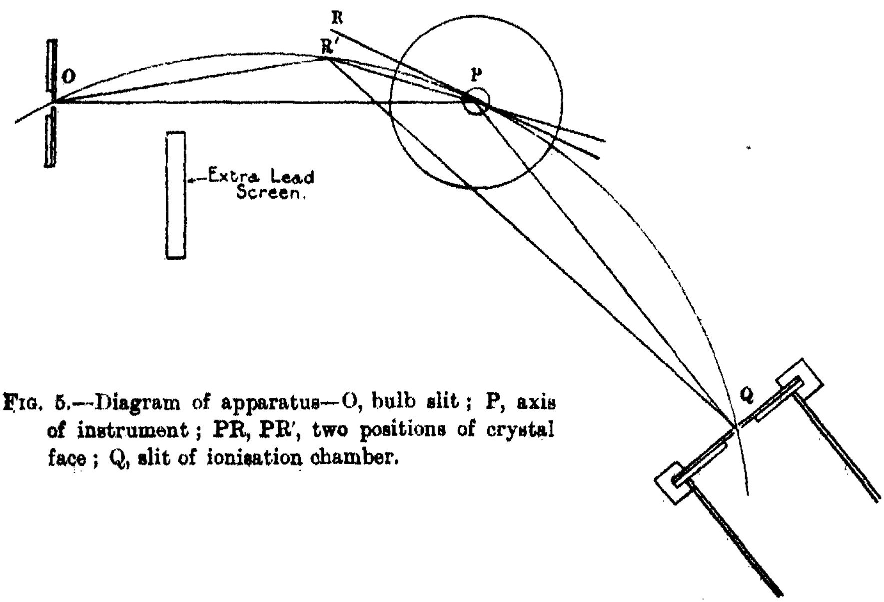


FIG. 5.—Diagram of apparatus—O, bulb slit; P, axis of instrument; PR, PR′, two positions of crystal face; Q, slit of ionisation chamber.

Here O is the bulb slit, P the axis of the instrument, and Q the chamber slit. When the crystal face is in the position PR, let us say, the ray OP

strikes at the right angle for reflection, and is reflected along PQ. But when the crystal is turned to OR′, the ray OP of the radiation of this quality which we are considering is not reflected at all. It is now the ray OR′, where R′ lies on the circle OPQ; for the angles made by OR′ and QR′ with PR′, and the angles made by OP and QP with PR, are all equal to each other. The ray OR′ is reflected along R′Q, and still enters the ionisation chamber, though the latter has not been moved. When, therefore, we see a maximum persisting in the same angular position of the chamber for several successive positions of the crystal, we know that we have a case of this special reflection. There is a relatively large quantity of very homogeneous radiation of a certain kind present in the radiation from the bulb. The narrower we make the slits the more does it stand out, but the more difficult it is to find, if we do not know where to look for it.

It will be noticed how small the general reflection appears, in comparison with the special reflection between the angles (crystal settings) 12° and 14°. It is still small when the angle is reduced to 10·7°. At 10·3° there is enough of it to throw a hump on to one side of a peak of special reflection, and at 9·9° it has passed through, and thrown the hump upon the other side. Consideration of the whole series of curves shows that there are three strongly marked homogeneous pencils of sharply defined quality; they occur at (uncorrected chamber angles) 27·7°, 23·4°, and 20·0°. What we have called the general reflection may comprise many other definite pencils, but they are scarcely resolved at all in this series of curves. Their presence is, however, fairly obvious. A series of potassium ferrocyanide curves shows them much more clearly. Three of this series are shown in fig. 4 (*a*), and their peculiar forms indicate to what extent interpretation has yet to be carried.

When these homogeneous beams are isolated by the use of narrow slits, it is possible to determine their absorption coefficients in various substances. In the end, there is no doubt, this will be done with great accuracy; for the present, our results must only be looked on as provisional. They are, perhaps, right to 5 per cent.; for many purposes this is quite sufficient. In the case of rock-salt we find the mass absorption coefficients in aluminium of A, B, and C to be 25·5, 18·8, and 10·6 respectively, the last being the most doubtful and probably too low. The absorption coefficient of the B-rays in Ag is 74, in Cu 140, in Ni 138; these values are approximate. We have made no exhaustive determination of the coefficients in the case of various crystals, but in a number of cases, all those tried, we have found them to be the same. There can be little doubt the three peaks are, in all cases, due to the same three sets of homogeneous rays, rays which do not change with the state of the bulb, but may well do so with the nature of the anticathode. It

will be observed that the absorption coefficient of the least penetrating set is very nearly that found by Chapman for the characteristic radiation of platinum.

The angles at which the special reflections of these rays take place are not the same for all crystals, nor for all faces of the same crystal, as the following table shows. The angles can be determined with great accuracy; even with our rough apparatus they are probably within 1 per cent. of the truth.

	A.	B.	C.
Rock-salt, cube face {100}	27·3	23·1	19·9
" face {111}	48·5	40·2	34·0
Potassium ferrocyanide	27·2	23·1	19·8
Calcite, cleavage plane {100}	25·4	21·6	—
Iron pyrites, cube face {100}	28·5	24·2	20·8
Zinc blende, cleavage plane {110}	40·0 (approx.)	33·0	27·5 (approx.)
Potassium bichromate	22·4	19·8	—

The readings for zinc blende and calcite are not corrected for errors of setting.

The difference in the case of the two faces of rock-salt suggested an attempt to find a repetition of the characteristic three peaks at multiples or sub-multiples of those at which they were first observed. For the sines of 11·55 and 20·1 (half the angles of the chamber settings of the B peak in the two cases) are 0·200 and 0·344 respectively. These are very nearly in the ratio $1 : \sqrt{3}$. If the effects are true diffraction effects such a relation might be expected. The {111} planes are further apart than the {100} planes in the ratio $2 : \sqrt{3}$; the sines of angles of special reflection should be in the inverse ratio, viz., $\sqrt{3} : 2$. True, the sines of the angles have been increased in the ratio $1 : \sqrt{3}$, instead of diminished in the ratio $2 : \sqrt{3}$, but it is not at all unlikely that a spectrum in one case is being compared with a spectrum of higher or lower order in the other. We, therefore, made a search for other spectra and found them at once. In the case of rock-salt we found traces of a third. The full rock-salt curves are shown in fig. 3 for the two kinds of face. The peaks first found are marked A_1, B_1, C_1, and their repetitions A_2, B_2, C_2; there is a trace of B_3 also. The corrected angular positions of B_1, B_2, B_3 are 23·1°, 47·3°, and 73·3°. The sines of the halves of these angles are 0·200, 0·401, and 0·597, and are very nearly in the proportion $1 : 2 : 3$. The absorption coefficient of the rays at B_2 is the same as that of the rays at B_1.

In the case of the rock-salt section {111} a spectrum occurs at half the angles first found. This is shown in fig. 3, II. It is not at all strongly

marked, and the question at once arises as to why the second spectrum should be so much stronger than the first in this case and so much weaker in the case of the face {100}. A large amount of the general falling away of intensity at small angles, so obvious in Curve II as compared with Curve I, is undoubtedly due to the fact that the {111} face used was not extended enough to catch the whole pencil of rays from the bulb slit at so glancing an angle.

There can be little doubt as to the interpretation of these results. The three peaks A, B, and C represent three sets of homogeneous rays. Rays of a definite quality are reflected from a crystal when, and only when, the crystal is set at the right angle. This is really an alternative way of stating the original deduction of Laue. The three sets of rays are not manufactured in the crystal, because all their properties are independent of the nature of the crystal. An absorbing screen may be interposed with the same effect before or after the rays have struck the crystal. This was found by Moseley and Darwin,* and we have verified it in the case of aluminium.

Since the reflection angle of each set of rays is so sharply defined, the waves must occur in trains of great length. A succession of irregularly spaced pulses could not give the observed effect. In the application of electromagnetic theory to monochromatic light on the one hand, and to homogeneous X-rays on the other, there is no difference to be considered beyond that of wave-length.

These results do not really affect the use of the corpuscular theory of X-rays. The theory represents the facts of the transfer of energy from electron to X-ray and *vice versâ*, and all the phenomena in which this transfer is the principal event. It can predict discoveries and interpret them. It is useful in its own field. The problem remains to discover how two hypotheses so different in appearance can be so closely linked together.

It is of great interest to attempt to find the exact wave-length of the rays to which these peaks correspond. On considering Curve I, fig. 3, it seems evident that the peaks $A_1 B_1 C_1$, $A_2 B_2 C_2$ are analogous to spectra of the first and second orders, because of the absence of intervening sets of peaks. The value of n in the equation

$$n\lambda = 2d \sin\theta$$

seems clear. The difficulty of assigning a definite wave-length to the rays arises when we attempt to determine the value of d, the distance of plane from plane.

* We learn that Messrs. Moseley and Darwin have lately been making experiments similar to some of those recorded here. Their results, which have not been published, agree with ours.

There is strong evidence for supposing that the atoms of a cubic crystal like rock-salt, containing two elements of equal valency, are arranged parallel to the planes $\{100\}$ in planes containing equal numbers of sodium and chlorine atoms. The atoms in any one plane are arranged in alternate rows of each element, diagonal to the cube axes, successive planes having these rows opposite ways. The question arises as to whether the value of d is to be taken as that between two successive planes, or two planes identical in all respects. The value of d in the one case is twice that in the other.

The centres of the atoms of sodium and chlorine, regarded for the time being as identical, are arranged in a point system, having as unit of its pattern a cube with a point at each corner and one at the centre of each cube face. The dimensions of this elementary cube can be found in the following way:—

If the side of the cube is of length a, the volume associated with each point in the point system will be $\frac{1}{4}a^3$.

The mass of a hydrogen atom being $1 \cdot 64 \times 10^{-24}$ grm. and the density of rock-salt $2 \cdot 17$, we have

$$\frac{1}{\frac{1}{4}a^3}\,\tfrac{1}{2}(35 \cdot 5 + 23) \times 1 \cdot 64 \times 10^{-24} = 2 \cdot 17.$$

This gives $$a = 4 \cdot 45 \times 10^{-8}.$$

The distance between planes passing through atoms identical in all respects is this distance a. The wave-length, as calculated in this way, is

$$\lambda = 2a \sin\theta = 1 \cdot 78 \times 10^{-8}$$

for the peak B.

But half-way between these planes which are identical in all respects are situated planes containing the same number of sodium and chlorine atoms, though the arrangement is not in all respects the same. Possibly this tends to make the odd spectra due to the first lot of planes disappear, and, if this is the case, we must halve the first estimate of the wave-length, and put

$$\lambda = 0 \cdot 89 \times 10^{-8}.$$

The difference between these two values corresponds to taking as a unit of the point system—

(1) The group 4NaCl, the smallest complete unit of the crystal pattern.

(2) The individual atom of either nature, associated with only one-eighth of the volume of the complete unit.

We have also examined the reflection from the (110) face of the rock-salt, and have found the peaks situated at such angles as indicate that the ratio of

the distance between these parallel planes to the distance between planes parallel to the face (100) is as $1:\sqrt{2}$. Combined with the position of the peaks reflected from the (111) face, this indicates that the point system which the diffracting centres form has as element of its pattern that suggested above, a cube with a point at each corner and one at the centre of each face. Of the three elementary cubic space lattices, this is the only one in which the distance between the (111) planes is greater than that between any other of the planes of the system.

The wave-length as calculated from the reflection on the (110) face of zinc blende agrees within the errors of experiment with that calculated above.

The wave-lengths to be associated with the spots in the photographs taken by Laue of the diffraction of X-rays by crystals are much smaller than these values. They belong to the region in which we have found reflection to take place at all angles, a region in which the peaks do not obviously occur. This agrees with the distribution of intensity amongst the spots.

The experimental method can be applied to the analysis of the radiation from any source of X-rays. It may, however, be able to deal only with intense radiations. The three sets of rays issuing from the bulb we have been using have angles of reflection whose sines are 0·236, 0·200, 0·173. The reciprocals of these are 4·24, 5, and 5·78. The frequencies, and therefore, according to Planck, the corresponding quantum energies, are in arithmetical progression. In this there is some hint of analogy with Rutherford's recent work on the energies of the various types of β-ray from RaC.

Prof. Barkla has lately communicated to the Physical Society an account of certain experiments in which a diffuse pencil of X-rays, when reflected on the cleavage plane of a crystal, acted on a photographic plate, producing a series of bands. The effect which we have been describing is clearly identical in part with that which Prof. Barkla has described. It is impossible, of course, to criticise a communication of which we have seen an abstract only. But it seems probable that the ionisation method can follow the details of the effect more closely than the photographic method has so far been able to do: and that in this way it is possible to distinguish between those bands which represent distinct sets of rays, and those which are repetitions of one and the same set.

Studies of the Processes Operative in Solutions. XXVIII.—*The Influence of Acids on the Rotatory Power of Cane Sugar, of Glucose and of Fructose.*

By F. P. Worley.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received April 15,—Read May 1, 1913.)

It is shown in Part XXII of this series of studies that when cane sugar is hydrolysed in the presence of solutions of sulphuric acid of different concentrations, the ratio of the final value of the rotation of the invert sugar to the initial value due to the cane sugar becomes very considerably greater as the concentration of the acid is increased. The effect was attributed to an increase in the optical rotatory power of the sugars caused by the acid; from the fact that the ratio of acid to sugar was the same in most of the experiments, it was argued that the determining factor was the ratio of acid to water, the alteration in the rotatory power being due mainly to changes in the water. Judging from the results of preliminary experiments and the work of previous investigators, it was probable that the fructose was the sugar chiefly affected but that the observed change in the above ratio could not be attributed to this cause alone.

In the course of experiments recently carried out to determine the hydrolytic activity of benzenosulphonic acid at different degrees of dilution, data have been accumulated which confirm the results arrived at when sulphuric acid was used as the hydrolyst. Experiments have also been carried out to determine the effect of the acid on the rotatory power of cane sugar, glucose and fructose.

It will be seen on reference to the following table that as the concentration of the acid is increased from one molecular proportion in two hundred of

Table I.

Mol. prop. of cane sugar.	Mol. prop. of hydrone.	Initial rotation.	Final rotation.	Ratio of final to initial rotation.
0·125	30	+ 9°·78	−3°·44	0·352
0·25	40	14°·92	4°·99	0·334
0·25	50	12°·43	4°·07	0·326
0·25	60	10°·68	3°·43	0·322
0·25	80	16°·60	5°·18	0·312
0·25	100	13°·52	4°·15	0·306
0·5	200	13°·96	4°·16	0·298

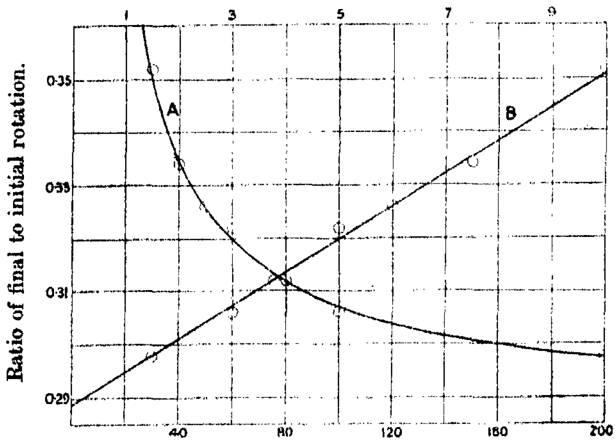
(Observations were made in the light of the mercury green line.)

"hydrone" (H_2O) to one in thirty, the ratio of the final negative rotation to the initial positive rotation is increased by about 17 per cent. In the experiments with from 30 to 60 molecular proportions of hydrone, polarimeter tubes two decimetres long were used and in the others tubes four decimetres long. One molecular proportion of acid was used throughout.

The results are set forth graphically in Diagram I. The values of the ratio of the final negative to the initial positive rotation are plotted as ordinates against the concentration of the acid as abscissæ. In Curve A the concentration is expressed in terms of the number of molecular proportions of hydrone to one of acid, and in Curve B as the number of molecular proportions of acid to 300 of hydrone.

Curve B is a straight line. The ratio of the rotation produced by the invert sugar to that of the original cane sugar in the absence of acid can be deduced by extrapolation to zero concentration of acid.

Mols. acid to 300 H_2O. (Curve B.)



Mols. H_2O to 1 of acid. (Curve A.)

DIAGRAM I.

In the experiments carried out to find the effect of acid on the rotatory power of cane sugar, glucose and fructose, the molecular proportions used were very approximately 0·25 of sugar and 40 of hydrone in the presence and absence of 1 of benzenesulphonic acid.

The cane sugar used was carefully purified coffee sugar, specially supplied by Messrs. Tate and Sons. Kahlbaum's first quality glucose and "crystallised" fructose were used. The water of crystallisation of the glucose was removed by desiccation *in vacuo* over concentrated sulphuric acid at 102° C. No special precautions were taken to purify the glucose and fructose, as the object of the experiments was to find the *change* in rotatory power caused

by the presence of the acid; judging from the rotatory powers arrived at, however, it is evident that there was little impurity present. The chief essential was that the samples used in the experiments with and without acid should not differ in rotatory power; to ensure this, a weighed quantity of the sugar was dissolved in water and portions of this solution were used in making up the solutions for the experiments. Care was taken that mutarotation was always complete. The same polarimeter tube was used throughout.

In order to deduce the value of the initial rotatory power of the cane sugar in the presence of the acid, it was necessary to make observations as soon after mixing as possible and by extrapolation to deduce the value of the rotation produced at the time of mixing. The solutions were contained unmixed in the mixing apparatus, described in Part XII, consisting of two 100 c.c. Jena conical flasks connected by a short wide U-tube ground into the necks. After being brought to 25° C. in the constant temperature air chamber described in Part XXII, the solutions were quickly mixed while still in the chamber, the time being noted; they were then immediately transferred to the polarimeter tube which was already at 25° on the water circuit. Readings of the rotatory power were taken at half-minute intervals and from these it was easy to find with a close approach to accuracy by extrapolation the value of the rotatory power at the time of mixing. The initial rotatory powers given above were obtained in this manner.

Table II.

Time in minutes after mixing	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0
Rotation	29·06	28·71	28·42	28·14	27·83	27·52	27·18	26·88

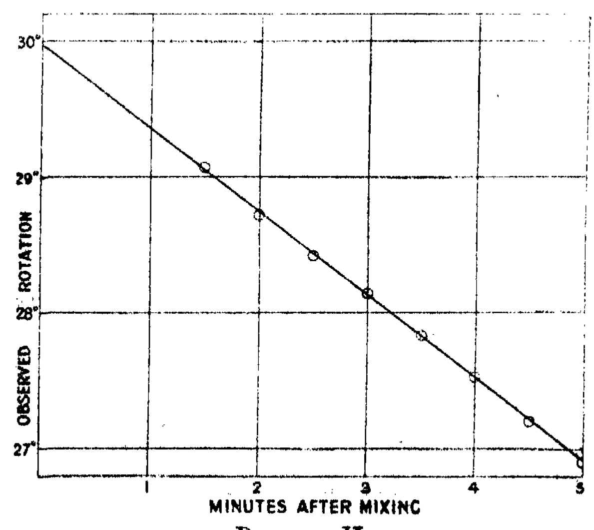


Diagram II.

The data in Table II, which are shown graphically in Diagram II, are derived from the experiment carried out to determine the rotatory power of cane sugar in the presence of benzenesulphonic acid and indicate the degree of accuracy of the method of finding the initial rotation by extrapolation.

Table III contains the experimental data and the deduced specific rotatory powers of cane sugar, glucose and fructose, in the presence and absence of benzene-sulphonic acid. The molecular proportions used were 0·25 of sugar, 40 of water and 1 of acid.

Table III.

	Observed rotation.	Density of solution.	Grm. of sugar per grm. of sol.	$[\alpha]^{25}_{Hg}$.
Cane sugar alone ...	+34°·505	1·03906	0·10605	+ 78°·28
" + acid	+29°·96	1·09429	0·08867	+ 77°·19
				Diff. 1°·09
Glucose alone	+14°·96	1·01961	0·05874	+ 62°·45
" + acid......	+12°·885	1·07903	0·04871	+ 61°·29
				Diff. 1°·16
Fructose alone	−25°·02	1·02002	0·05874	−104°·40
" + acid ...	−22°·84	1·07937	0·04873	−108°·56
				Diff. 4°·16

It will be observed that the change in specific rotatory power caused by the acid is in the same direction in the case of all three sugars, *viz.*, a decrease in positive or an increase in negative rotation, the change being considerably greater in the case of fructose than in that of cane sugar or glucose. Moreover, in each case, the change would increase the value of the ratio of the final negative rotation of the invert sugar to the initial positive rotation of the cane sugar in the experiments described above. Furthermore, omitting in each case any mutual effect that glucose and fructose may have on their individual specific rotatory powers, the specific rotatory power of invert sugar in the absence and presence respectively of acid would be

$$\frac{62{\cdot}45-104{\cdot}40}{2}\ (=20{\cdot}975)\quad\text{and}\quad\frac{61{\cdot}59-108{\cdot}56}{2}\ (=23{\cdot}635).$$

The value of the ratio found when the molecular proportion of water to acid was 40 to 1 was 0·334. In the absence of acid, therefore, it should be

$$\frac{0{\cdot}334}{1}\times\frac{77{\cdot}19}{78{\cdot}28}\times\frac{20{\cdot}975}{23{\cdot}635}=0{\cdot}292.$$

This value is practically identical with that found from Diagram I by extrapolation to zero concentration of acid, viz., 0·289; that found when sulphuric acid is used is 0·290.

It is therefore clear that the large alteration produced by the acid in the value of the ratio of the final to the initial rotation in the experiments on the hydrolysis of cane sugar can be completely and satisfactorily explained by the changes produced by the acid in the rotatory powers of the three sugars involved.

The Decrease in Velocity of α-Particles in Passing through Matter.

By E. MARSDEN, M.Sc., Lecturer, and T. S. TAYLOR, Ph.D., John Harling Fellow, University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received April 22,—Read May 1, 1913.)

It is becoming recognised that one of the most fruitful sources of information as to the internal structure of atoms is provided by the phenomena attending the passage of swift electrified particles through them. In particular from a consideration of the scattering of α-particles it has been found that the atom consists essentially of a very concentrated charge at the centre of the atom* surrounded by electricity of the opposite sign, probably electrons, distributed throughout the remainder of the atom. Further, Darwin† and Bohr‡ have attempted to obtain information as to the number and distribution of electrons in the atom by a consideration of the absorption or loss of velocity of the α-particles in passing through matter. The only data for this purpose so far obtainable are provided by the velocity curves, or relations between velocity and thickness of matter traversed, in aluminium as determined by Rutherford,§ and in mica as determined by Geiger.‖ It seemed, therefore, of interest to make a more complete investigation of the velocity curves in various substances, more particularly as the earlier observations are subject to slight errors due to the assumption that equal thicknesses of matter have the same air equivalent at different parts of the range of α-particles.

In the present experiments the velocity curves in gold, copper, aluminium, mica and air have been determined, using as source the α-particles of

* E. Rutherford, 'Phil. Mag.,' 1911, vol. 21, p. 669.

† C. G. Darwin, 'Phil. Mag.,' 1912, vol. 23, p. 907.

‡ N. Bohr, 'Phil. Mag.,' 1913, vol. 25, p. 10.

§ E. Rutherford, 'Phil. Mag.,' 1906, vol. 12, p. 138.

‖ Geiger, 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 505.

radium C as in the experiments of Rutherford and of Geiger. The velocities of the α-particles before and after passing through sheets of matter of various thicknesses were measured by the deflection of the α-particles in a known magnetic field. The apparatus used is shown in fig. 1. It consists essentially of a source of radiation D, a series of absorption foils T, a slit L, to form a pencil of the α-particles, and a zinc sulphide screen M on which the position of the pencil could be observed, the whole being enclosed in an evacuated chamber C between the poles of a large electromagnet.

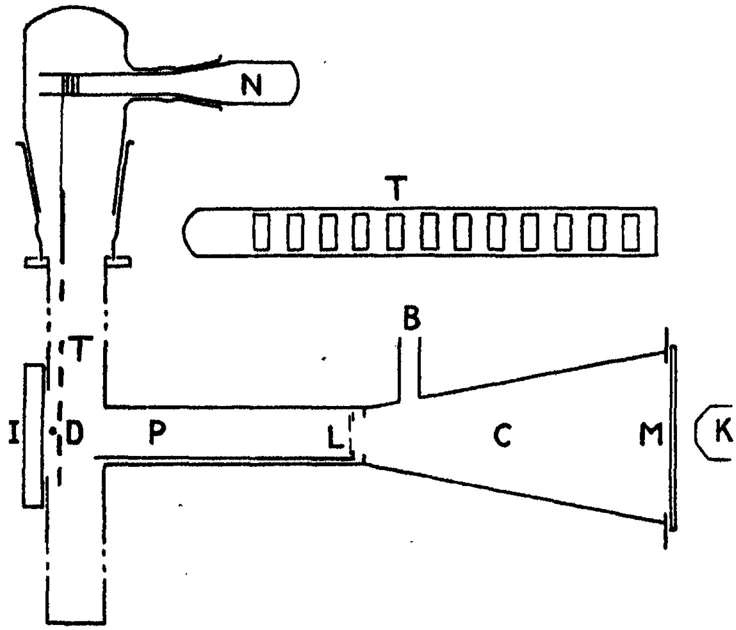


FIG. 1.

The source consisted of a fine platinum wire 1·5 cm. in length and 0·15 mm. in diameter which had been exposed to a strong source of radium emanation so as to become activated with a deposit of about 20 millicuries radium C. Twenty minutes after the wire was withdrawn from the emanation the radium A had practically disappeared, so that the α-particles emitted came from radium C only. The source fitted with its ends in a support attached to the platform P, which also held the slit L, the wire being adjusted so as to be parallel to the slit and about 8 cm. from it. The platform could be slipped into the brass chamber and against a stop as shown in the figure, the opening being closed by a ground glass plate I, and the whole evacuated through a tube B by means of a Fleuss pump and cooled charcoal.

The foils whose absorption was under investigation were placed over windows in a "ladder" T, and by means of a piece of thread attached

round a tube projecting from a ground-glass joint N any particular window could be placed opposite the source without altering the exhaustion in any way. The absorption foils were weighed in the form of single sheets and a number of layers taken, so that successive windows differed from one another by convenient amounts. In all cases the air equivalents of the windows were also obtained by the scintillation method, these measurements affording a useful check on the weighings.

The pencil of α-particles passed through the slit and fell on the zinc sulphide screen, producing a fine line of scintillations, the position of which could be easily read to 1/20 mm. by means of a travelling microscope K. The magnetic field was then applied perpendicular to the plane of the diagram and the position of the line of scintillations again read. The successive windows were then moved in front of the source and the new positions of the line of scintillations determined. Similar observations were made with the same value of the magnetic field, but reversed, and the double deflections obtained by subtracting the corresponding readings. Measurements were continued with different field strengths up to 9000 gauss, until the radium C had decayed to such a small activity that observations were difficult to make. The relative velocities were calculated by substituting in the formula $mv/e = H\rho$, where m, v, and e are the respective values of the mass, velocity, and charge of the α-particles, H the field strength and ρ the radius of curvature of the path of the particles obtained from the relation $4\rho^2d^2 = [b^2+d^2][d^2+(a+b)^2]$. In the latter formula d is the deflection produced by the magnetic field as measured on the screen, and a and b the distances of the slit from the source and screen respectively. This formula applies to the experiments, as the whole of the path of the particles was in the magnetic field, which was uniform to less than 1 per cent. throughout the whole of its length. In all cases the ratios of the velocities, with and without absorption sheets, were calculated, and these are practically inversely proportional to the double deflections in the same magnetic field, a small correction being necessary, depending on the magnitudes of the deflections. An example of a set of readings is given in Table I.

The velocity curve obtained in the case of gold is shown in fig. 2, where the ordinates represent relative velocities and abscissæ the mass per unit area, or thickness × density, of the foils used. For foils greater than about 6 cm. air equivalent the velocity changes rapidly with thickness, and the method generally adopted was to place a foil of about 5·5 cm. air equivalent directly over the source, and to use additional foils for the windows of the "ladder" increasing in thickness by very small amounts.

Table I.—Gold Foils. Example of a set of readings.

Exciting current of magnet.	Mass per unit area of "window."	Double deflection.	Relative velocity.
ampère.	grm.	cm.	
1	—	0·685	1·0
1	$9\cdot63\times10^{-3}$	0·78	0·814
1	13·44	0·825	0·770
1	18·10	0·94	0·675
1	22·90	1·23	0·516
1	25·43	1·395	0·455
5	—	2·841	1·0
5	$2\cdot88\times10^{-3}$	2·96	0·962
5	4·31	3·032	0·940
5	6·25	3·12	0·915
5	9·63	3·515	0·817

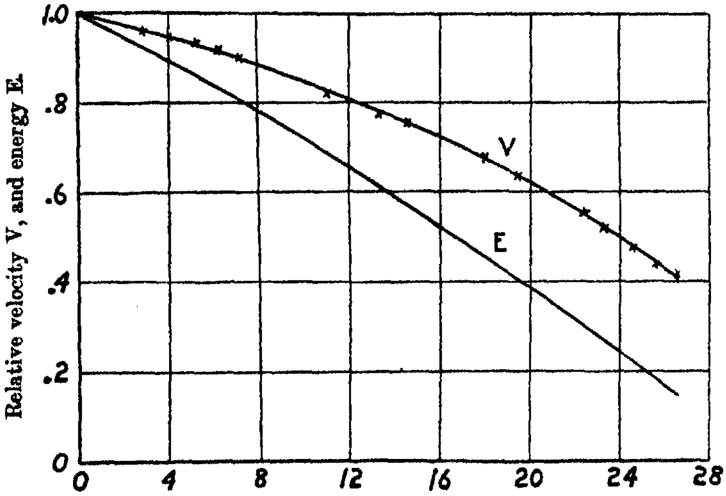


FIG. 2.

The curve shown is seen to be smooth down to a velocity of 0·415 of the initial velocity corresponding to a mass per square centimetre of 0·0266 grm., or an air equivalent of 6·5 cm. at 15° C. and 76 cm. Hg. Here a somewhat unexpected difficulty was encountered, for with additional thickness of foil no further diminution in velocity could be detected. The line of scintillations apparently remained stationary although steadily decreasing in intensity with increasing thickness. Similar results were obtained with Cu, Al, and mica; in no case could we obtain with certainty a velocity less than about 0·415 of the initial velocity of expulsion. This question will be discussed more fully in a later section of the paper.

Table II gives the results of the experiments, the masses per unit area of

the various materials being given which were necessary to cut down the velocity of the α-particles to the fractions given in column 1. The values are taken from smooth curves drawn through the experimental points. For gold and mica the values are probably correct to 1 per cent., although the results for copper and aluminium are not quite so reliable, owing to the unhomogeneity of the foils used. As the velocity changes comparatively slowly with the thickness, especially for thicknesses up to about 3 cm. air equivalent, the values of the velocity corresponding to any given thickness will have a considerably greater percentage accuracy. The foils were in all cases commercially pure. The values given for velocity 0·415 are taken from the curves as the smallest mass per square centimetre necessary to give this velocity. The values given in the last line of the table are the masses per square centimetre necessary to completely absorb the α-particles in the various materials. These numbers were not determined directly, but by extrapolation from the values necessary to cut down the range by about 6·5 cm. in air, using for the remainder of the range the numbers given by Richardson and one of us.* The method by which the values for air given in the last column were obtained is given in the next section.

Table II.

Relative velocity.	Mass per unit area × 10^3 grm.				
	Gold.	Copper.	Aluminium.	Mica.	Air.
1·0	—	—	—	—	—
0·95	4·00	2·08	1·48	1·43	1·24
0·90	7·05	3·90	2·79	2·75	2·32
0·85	9·79	5·35	3·94	3·83	3·26
0·80	12·27	6·69	5·01	4·86	4·08
0·75	14·80	8·00	6·05	5·72	4·84
0·70	17·04	9·20	7·03	6·40	5·46
0·65	18·99	10·30	7·85	7·00	6·02
0·60	20·71	11·40	8·50	7·50	6·48
0·55	22·29	12·35	9·10	7·98	6·90
0·50	23·89	13·13	9·64	8·47	7·29
0·45	25·40	14·00	10·15	8·96	7·67
0·415	26·65	14·60	10·46	9·35	7·96
End	29·50	16·00	11·40	10·15	8·50

In connection with the above experiments the value of mv/e for the unabsorbed α-particles was determined by substitution of the various values in the formulæ given above. The distances of the source from the slit and screen were 8·185 and 16·565 cm. respectively. With six values of the field varying between 4000 and 8500 gauss, the values of mv/e determined

* Marsden and Richardson, 'Phil. Mag.,' 1913, vol. 25, p. 184.

from the observed deflections were 4·00, 4·00, 3·99, 4·00, 4·00, $4·015 \times 10^5$ electromagnetic units respectively, with a mean of $4·00 \times 10^5$. The concordance of these results shows the sensitiveness of the method of measurement. The mean result is probably correct to ½ per cent., an uncertain error arising from the details of the ordinary laboratory instruments used in the calibration. An accurate investigation of initial velocity and e/m is at present in progress by Prof. Rutherford and Mr. Robinson in this laboratory. In two experiments values were obtained of the relative velocity of the α-particles from radium A by making the observations within a few minutes after withdrawing the source from the emanation. The mean value obtained was 0·882 of the velocity of the radium C α-particles, and this value is in excellent agreement with the value deduced from the known ranges.*

Velocity Curve in Air.

If a foil is taken of air equivalent a, and which reduces the velocity of an α-particle to a fraction ρ, then a, ρ is a point on the air velocity curve. Consequently, by plotting the air equivalents of the foils used in the above determinations against the velocities of the emergent α-particles, the air velocity curve can be determined. The values obtained from the curves for gold and mica are given in Table III, where columns 2 and 3 give the air equivalents at 15° C. and 76 cm. Hg of the foils corresponding to the relative velocities given in column 1.

Table III.—Velocity Curve in Air, 15° C. and 76 cm. Hg.

Velocity.	Air values as deduced from—		Experimental air value.	Weighted mean.	Value deduced from formula $v^3 = aR$.
	Gold.	Mica.			
	cm.	cm.	cm.	cm.	cm.
1·0	—	—	—	—	—
0·95	1·02	1·00	1·02	1·01	0·99
0·90	1·85	1·92	1·87	1·89	1·88
0·85	2·64	2·68	2·67	2·66	2·68
0·80	3·28	3·35	3·30	3·33	3·39
0·75	3·89	3·98	3·95	3·95	4·01
0·70	4·40	4·47	4·47	4·46	4·56
0·65	4·87	4·92	4·92	4·91	5·03
0·60	5·29	5·27	5·40	5·29	5·44
0·55	5·65	5·62	5·75	5·63	5·79
0·50	6·00	5·92	6·10	5·95	6·07
0·45	6·30	6·25	6·35	6·26	6·31
0·415	6·50	6·50	6·48	6·50	6·44
End	6·94	6·94	6·94	6·94	6·94

* *Cf.* Geiger and Nuttall, 'Phil. Mag.,' October, 1912, vol. 24, p. 647.

It is assumed in using the above data that the α-particles are absorbed similarly by the various materials, *i.e.* either that the emergent α-particles are homogeneous in velocity or that they are "straggled" or sorted out in velocities to the same extent. This question has been discussed by Richardson and one of us (*loc. cit.*), and further evidence will be given in the next section of this paper. It appears to us that we are justified in obtaining the air velocity curve in this way, at any rate to an accuracy within the possible experimental error, especially for velocities above 0·5 of the initial velocity. A difficulty arises in measuring the air equivalents of foils greater than that corresponding to about 6·5 cm. If the experiment is done in air at ordinary pressure either by ionisation or by the scintillation method this difficulty is due to the large variation in intensity of the α-particles at the end of the range with the source uncovered (*i.e.* at about 7 cm. distance), and the end of the range when such a thick foil is interposed (*i.e.* less than 1 cm. distance). In our experiments the scintillation method was used, with radium C as source. A zinc sulphide screen was adjusted at the end of the range with and without the various foils interposed. For the very thick foils the source was sometimes allowed to decay to a small intensity before making the adjustment with the foil covering the source. The difference between the distances of the zinc sulphide screen from the source with and without the foil over it gives the air equivalent required. As a check on the values for the thicker foils the source, foils, and screen were enclosed in a chamber which could be evacuated. A constant distance separated the source and the screen, and the pressure was adjusted until the α-particles just failed to reach the screen. Even with these precautions a difficulty was encountered owing to the unhomogeneity of the foils, and for this reason more reliance is placed on the values obtained with mica.

The values are all reduced to 15° C. and 76 cm. Hg. The masses per unit area corresponding to any air equivalent are in general a few per cent. less than the values determined by Richardson and one of us from the variation of air equivalent along the range of foils of the order of 1 cm. air equivalent. For this reason the masses given by these authors for the equivalents per centimetre at various points of the range will require diminishing by a factor constant for each substance.

A direct determination of the air velocity curve was also made, although owing to the nature of the experiment the values obtained are probably not quite so accurate as those deduced by the above method. The apparatus of fig. 1 was used, the slide holding the source and slit being modified as shown in fig. 3. The plate P held a fine slit S_1 covered airtight by a thin mica window equivalent to about 0·9 cm. air, and the whole was waxed so as to

cover the opening (I in fig. 1) also airtight. The source was placed at W at a definite distance from S_1, and a bell-jar fitted air-tight over S_1 and the plate P. The slide carried a second slit S_2 in line with S_1 and W.

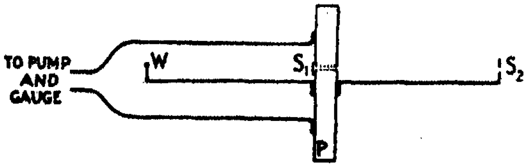


FIG. 3.

The main chamber was evacuated completely, and the pressure varied in the bell-jar. In this way the range of the α-particles entering the magnetic deflecting chamber could be varied. The air equivalent of the mica window was known at different parts of the range, and by adding the equivalent at 15° and 76 cm. Hg. of the air between W and S_1 at the various pressures the exact reduction of range could be calculated. The reason that two slits were necessary arose from the considerable "compound" scattering of the beam of α-particles, which would otherwise cause a spreading out of the pencil received on the zinc sulphide screen. Even with the above arrangement a certain amount of spreading of the beam due to scattering is unavoidable, and also for the same reason there is a considerable reduction in the intensity of the α-particles for low velocities where the scattering becomes considerable. Thus measurements of a high degree of accuracy could not be obtained by this method. The results are given in Column 4 of Table III, and they prove the substantial accuracy of the values calculated by the former method. As in the experiments with metal foils no certain evidence could be obtained of velocities below 0·415 of the initial velocity.

Attempts to Obtain Velocities below 0·41 *of the Initial Velocity.*

It has already been mentioned that with foils of any material, of thickness from 6·5 cm. air equivalent upwards, no reduction in velocity could be obtained below 0·415 of the initial velocity. This result is in agreement with Prof. Rutherford's original experiments (*loc. cit.*), in which a lower limit of 0·43 was obtained. Rutherford used aluminium foils and a photographic plate to register the deflected bands of α-particles, and it has generally been assumed that his failure to obtain low velocities arose from the want of uniformity of his foils. Geiger (*loc. cit.*), using mica as absorbing substance and the scintillation method, obtained two values of velocity as low as 0·39 and 0·27 of the initial velocity respectively.

Observations at the end of the range are difficult owing to several causes: Firstly, there is a rapid decrease in the number of α-particles which penetrate foils of air-equivalent greater than about 6·5 cm. This decrease arises from the phenomena of compound scattering, for the most probable angle of scattering* for sheets of gold and mica of 6·5 cm. air-equivalent are of the order 20° and 5° respectively, and the scattering will then increase very rapidly with increasing air equivalent. Consequently, only a fraction of the α-particles will emerge from such foils, due to the increased distance traversed in an oblique direction through them, and it would also be expected that there would be a variation in velocity in the α-particles which do emerge. Further, not only is the number of α-particles in the beam greatly reduced, but the brightness of the scintillations themselves decreases considerably, and observation becomes difficult.

From these considerations it will be seen that for low velocities it is necessary to use a very intense source, and to place uniform absorption sheets directly over it so as to keep the spreading of the beam at a minimum. However, with these precautions, and using the arrangement of sliding absorption windows, we were unable, as has already been stated, to obtain velocities below 0·415 of the initial velocity. In all cases the deflection caused by a magnetic field remained constant for foils greater than 6·5 cm. air equivalent. An experiment was tried in which the increase of thickness was obtained by rotating a sheet of mica of about 6 cm. air-equivalent about an axis parallel and very near to the source. The same result was obtained; after a certain rotation the deflected beam remained stationary until it was too faint to observe. This result was obtained whether the whole of the apparatus was in the magnetic field or only that part from the slit to the zinc sulphide screen.

In another experiment the apparatus was cut down to half its length, and a source of radium C equivalent to the amount in equilibrium with 15 millicuries of radium emanation was used, on a wire of 1/10 mm. diameter, with a slit 1/10 mm. wide. Three foils of mica, equivalent to 6·5, 6·6, and 6·8 cm. of air, were employed successively and placed directly over the source with a separate evacuation for each experiment. The resultant double deflections were 3·35, 3·33 and 3·25 mm. respectively, and the double deflection for the bare wire was 1·40 mm. These values are constant within the limits of experimental error due to the extreme faintness of the bands, the mean value of the velocity being 0·42 of the velocity with the source uncovered. The cross wire in the microscope was set in each case on the centre of the band of scintillations.

* H. Geiger, 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 492.

Owing to the faintness of the bands there was some difficulty in estimating any possible unhomogeneity in velocity. However, the deflected band appeared narrower for the greater thicknesses. For the mica equivalent to 6·5 cm. the measurements indicated that α-particles of 39 to 47 per cent. of the initial velocity were present. However, a lower limit of velocity was not at all evident even with the thicker micas.

Discussion of Results.

It will be more convenient first to discuss the results of the last section. It is possible that in the beam of α-particles after passing through 6·5 cm. air-equivalent, the velocities are distributed within the limits 39 to 47 per cent., just mentioned. With further absorption the particles of higher velocities may become degraded in velocity. However, we are faced with the difficulty of accounting for the absence of α-particles of lower velocities. It is possible that they no longer produce scintillations. This point was investigated with different zinc sulphide screens but with negative results. But even if they no longer produce scintillations then it is probable that they also no longer ionise, for the ranges of α-particles determined by the scintillation method are the same as those determined by the ionisation method.

The results may possibly be explained by assuming that when the velocity of an α-particle falls below a certain value it is subject to a new special type of scattering, possibly by some kind of sub-central charge present in the atom. From an examination of the large number of α-particles in the photographs of C. T. R. Wilson* which exhibit large angle deflections in the last 2 mm. of the range as shown by the cloud trails we have calculated that this number is far in excess of the number to be expected on the laws of single scattering of Rutherford,† experimentally proved by Geiger‡ and one of us. However, with such an hypothesis one might expect some difference in the limiting velocity with different substances unless it is supposed that the same sub-centres are present in all atoms.

An alternative explanation may, of course, be obtained on the assumption that at this particular velocity the α-particle takes on an electron and then has only one positive charge. This would account for the limiting velocity coming practically the same in all the substances. An attempt was made to detect such singly charged α-particles but only one line of scintillations in the magnetically deflected beam could be observed.

It must be remembered, however, that Geiger apparently obtained one

* C. T. R. Wilson, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 277.

† E. Rutherford, 'Phil. Mag.,' 1911, vol. 21, p. 669.

‡ H. Geiger and E. Marsden, 'Phil. Mag.,' 1913, vol. 25, p. 604.

value of the velocity as low as 0·27. We tried to repeat his conditions but were unable to obtain such a low velocity. Whether Geiger's result may prove correct or not there must be some very radical change accompanying the absorption of the α-particles when their velocity falls to 0·41 of the initial velocity (radium C).

We now turn to the discussion of the figures given in the first section of the paper for the velocity curves in the various materials. For the air-velocity curve Geiger deduced from his results the formula $V^3 = aR$, where V is the velocity, a a constant and R the range of the α-particles emerging from the absorbing foil. Putting in the value 6·94 for the total range at 15° and 76 cm. Hg, the values given in Column 6 of Table II were deduced and it will be seen that except for velocities less than 0·41 they show a good agreement with the experimental values. With regard to the velocity curves in other materials the formula does not hold, the curve approaching more nearly to that expressed by $V^2 = aR$ for substances of increasing atomic weight. This is indicated by the energy curve for gold shown in fig. 1.

Darwin (*loc. cit.*) first attempted to deduce expressions for the velocity curve in various materials, the assumption being that the α-particle loses energy by setting in motion the electrons in the atoms of the absorbing substance. To avoid, as far as possible, any hypotheses as to the structure of atoms Darwin also assumed that an α-particle only acts on the electrons in an atom when it actually passes through the atom. Bohr has extended Darwin's results and removed the objection of limiting the action of the α-particle. Bohr arrives at a formula which may be reduced to

$$\frac{dV}{dx} = -\frac{A}{v^3}\left\{\frac{B}{A}\log V + 1\right\}^*,$$

where v is the velocity of an electrified particle, x the distance traversed through the absorbing material and A and B are constants. We have applied this formula to our results, but the agreement is only good for velocities greater than about 0·6 of the initial velocity. This, however, does not altogether contradict the theory, for certain assumptions used by Bohr in integrating his formula do not hold for low velocities. For instance, the formula depends on the assumption that a certain distance $\lambda\,[= eE(M+m)/V^2mM]$ exists, which is very small in comparison with

* Bohr's actual formula is $\frac{dV}{dx} = -\frac{4\pi e^2E^2N}{mMV^3}\sum_{s=1}^{s=r}\log\left(\frac{V^3kMm}{n_s eE(M+m)}\right)$. E and M are the charge and mass of the electrified particle, e and m the corresponding quantities for an electron. N is the number of atoms per unit volume, and k a constant = 1·123. The frequencies of the r electrons in each atom are denoted by $n_1, n_2, \ldots n_r$.

V/n. This assumption comes in in the consideration of the effect of the atomic forces on the motion of the electrons disturbed by an α-particle.

If we consider the variation in the velocity of an α-particle when $V/V_0 = 0{\cdot}5$, say, *i.e.* $V = 1{\cdot}0 \times 10^9$, it can be calculated that n must be extremely small compared with $2{\cdot}0 \times 10^{18}$ for this assumption to hold. For oxygen, Bohr calculates from data of Planck and of Whiddington that for some electrons in the atom $n = 1{\cdot}1 \times 10^{18}$, and that for materials of higher atomic weight electrons of much higher frequencies must exist. Thus Bohr's conditions probably do not hold for low velocities, and this possibility he has himself already pointed out.

It is interesting to note that no theoretical explanation has so far been given for Bragg's law that the absorption of α-particles per atom of different substances is proportional to the square root of the atomic weight. This law is not strictly accurate, as it cannot hold for all velocities of α-particles, yet its wide range of approximate application seems to suggest that it has some simple theoretical foundation.

We are deeply indebted to Prof. Rutherford for his helpful encouraging interest in these experiments, and for supplying us with the large quantities of radium emanation necessary.

Synthesis of the Anhydrides of α-Aminoacyl Glucosamines.

By Charles Weizmann and Arthur Hopwood.

(Communicated by Dr. A. Harden, F.R.S. Received April 5,—Read June 19, 1913.)

The behaviour of the albumin glucosides and the mucus bodies known as *mucins*, *mucinogens*, *mucoids*, and *hyalogens*, on hydrolysis suggests the probability that these complex proteins would bear the same relation to the condensation products of the sugars or the amino-sugars with the amino-acids as the simpler proteins bear to the polypeptides. Consequently, the authors decided two years ago to make a start in the synthesis of the glucoproteins by preparing the condensation products of glucosamine with the amino-aliphatic acids, in order that their properties and behaviour towards ferments could be ascertained and compared with those of the degradation products of the glucoproteins and thereby throw some light on the constitution of these complex and important organic bodies.

After many failures, the method of synthesis which we eventually adopted for the condensation of glucosamine with amino-aliphatic acids was somewhat similar to one of the methods employed by Emil Fischer and his co-workers* in the synthesis of the polypeptides. In brief, the method consists in condensing α-bromoacyl haloids with glucosamine hydrochloride in the presence of sodium hydroxide, and then displacing the halogen in the resulting α-bromoacyl glucosamines by an amino-group through the action of cold aqueous ammonia, viz.:—

$$\begin{array}{c}\text{α-Bromoacyl Haloid} + \text{Glucosamine Hydrochloride.}\\ \text{sodium}\downarrow\text{hydroxide.}\\ \text{α-Bromoacyl Glucosamine.}\\ \text{aqueous}\downarrow\text{ammonia.}\\ \text{Anhydride of α-Aminoacyl Glucosamine.}\end{array}$$

Numerous difficulties were encountered in carrying out these changes. In coupling the α-bromoacyl haloids with glucosamine hydrochloride in the presence of sodium hydroxide, it was found that good yields were obtained only when molecular proportions of the reacting substances were employed and when the mixture was vigorously shaken and maintained about the temperature of melting ice. Further, in the subsequent treatment of the α-bromoacyl glucosamines with aqueous ammonia, the temperature had also

* 'Ber.,' 1903, vol. 36, p. 2982, *et seq.*

to be kept low both during the interaction of the bodies and the subsequent evaporation under reduced pressure, otherwise much decomposition took place and sticky brown masses resulted.

It should be observed here that when molecular proportions of α-bromoacyl haloids and glucosamine hydrochloride are condensed together in the presence of cold alkali hydroxide, the whole of the bromoacyl group of the substituted acid chloride appears to unite with the amino-group and none with the hydroxyl groups of glucosamine. This is shown by the fact that the condensation product made from molecular proportions of α-bromolauryl chloride and glucosamine hydrochloride in the presence of normal sodium hydroxide is practically insoluble in dilute or concentrated hydrochloric acid, an almost conclusive proof that only the amino-group present in glucosamine is attacked when the condensation process is carried out under the above conditions. Moreover, this view is also supported by the analogous behaviour of the α-bromoacyl haloids towards serine, isoserine, tyrosin, and other hydroxyamino-acids in the presence of alkali hydroxides.*

It should also be noted that when the α-bromoacyl glucosamines interact with cold aqueous ammonia, they do not yield the expected α-aminoacyl glucosamines but the anhydrides of α-aminoacyl glucosamines. The action appears to consist in the replacement of the bromine atom in one molecule of the α-bromoacyl glucosamines for an amino-group, and the simultaneous or subsequent withdrawal of the elements of water. The analyses of the products formed by the action of ammonium hydroxide on α-bromopropionyl glucosamine and α-bromoisohexoyl glucosamine demand this conclusion. Moreover, it seems that whenever ammonia or alkalies act upon glucose or its derivatives the change which takes place is generally accompanied by the loss of a molecule of water.†

In concluding this introduction, we should state that since we published a preliminary note on the condensation of α-bromoacyl haloids with glucosamine,‡ we find that other chemists have also been working simultaneously on the derivatives of glucosamine with a view to developing the synthetic chemistry of the glucoproteins.§ We should like to state that we are experimenting from an entirely different point of view, and no overlapping has so far

* *Cf.* E. Fischer, 'Ber.,' 1904, vol. 37, pp. 2486–2571; *ibid.*, 1907, vol. 40, pp. 3704–3717; E. Fischer and W. F. Koelker, 'Ann.,' 1905, vol. 340, pp. 180–190; E. Fischer and H. Roesner, 'Ann.,' 1910, vol. 375, pp. 199–206.

† *Cf.* Lobry de Bruyn, 'Ber.,' 1895, vol. 28, p. 3082; Emil Fischer and Karl Zack, 'Ber.,' 1912, vol. 45, pp. 456–465, 2068–2074.

‡ *Cf.* A. Hopwood and C. Weizmann, 'Chem. Soc. Proc.,' 1912, vol. 28, p. 261.

§ *Cf.* J. C. Irvine and A. Hynd, 'Trans. Chem. Soc.,' 1913, vol. 103, pp. 41–46.

taken place either in the methods adopted or in the products obtained by synthesis.

α-Bromopropionyl Glucosamine, $CH_3 \cdot CHBr \cdot CO \cdot NH \cdot C_6H_{11}O_5$.

α-Bromopropionyl glucosamine is prepared by the condensation of α-bromopropionyl bromide and glucosamine hydrochloride in cold alkaline solution. For this purpose, 4 grm. of α-bromopropionyl bromide (1 mol.) and 18·6 c.c. of N sodium hydroxide (1 mol.) are added gradually and alternately, with vigorous shaking after each addition, to a well-cooled solution containing 4 grm. of glucosamine hydrochloride (1 mol.) dissolved in 18·6 c.c. of N sodium hydroxide (1 mol.). There is much frothing and a colourless precipitate separates out immediately after the condensation begins to take place. The mixture is kept cool for about two hours by surrounding the containing vessel with melting ice, and when the odour of α-bromopropionyl bromide has disappeared a slight excess of concentrated hydrochloric acid is added. After standing for about 30 minutes, the impure α-bromopropionyl glucosamine is collected, washed with a little cold water, and dried in air on a porous plate. A further crop of crystals is obtained by evaporating the mother liquor at ordinary temperatures, which like the former are purified by recrystallisation from hot absolute alcohol. Total yield, 4·1 grm.

α-Bromopropionyl glucosamine crystallises from alcohol in colourless prismatic needles which melt and decompose at 200–201° when slowly heated, and at 210–211° when quickly heated, yielding a black liquid. The crystals are readily soluble in hot and moderately soluble in cold water. They are readily soluble in dilute alcohol (50 per cent.), but are difficultly soluble in cold and only moderately soluble in hot absolute alcohol. They are insoluble in ether, but dissolve instantly in cold ammonia or alkali hydroxides, forming yellow solutions. The warm aqueous solution of α-bromopropionyl glucosamine readily reduces alkaline copper solutions, yielding red copper oxide, or ammonio-silver nitrate solution, giving a silver mirror; but when an aqueous solution of the bromide is shaken and warmed for two hours with a little more than one molecular proportion of either semicarbazide hydrochloride dissolved in excess of sodium acetate solution or phenyl hydrazine dissolved in dilute acetic acid no semicarbazone or phenylhydrazone is formed, and the resulting solutions on evaporation under reduced pressure yield most of the original bromide unchanged.

0·6201 gave 24·1 c.c. N_2 at 14·0° C. and 751 mm. N = 4·57.
0·1793 „ 0·1073 AgBr. Br = 25·47.
$C_9H_{16}O_6NBr$ requires N = 4·46; Br = 25·45 per cent.

Alanyl Glucosamine Anhydride, $C_9H_{16}O_5N_2$.

Alanyl glucosamine anhydride is prepared by the action of cold ammonium hydroxide on α-bromopropionyl glucosamine. For this purpose 1 grm. of α-bromopropionyl glucosamine is mixed with excess of concentrated aqueous ammonia in a pressure bottle and then shaken for five days at the ordinary temperatures of the laboratory. The resulting solution is evaporated whilst cold in a vacuum desiccator over concentrated sulphuric acid until crystals of impure alanyl glucosamine anhydride separate out, which are then collected and washed with cold absolute alcohol in order to remove brown decomposition products. Further crops of crystals are obtained by evaporating the aqueous mother liquor and the alcoholic washings at ordinary temperatures under reduced pressure. The crude products are then dissolved in hot water and boiled with animal charcoal until the solution becomes colourless. On cooling, alanyl glucosamine anhydride separates from the aqueous solution in colourless prismatic needles, which are further purified by recrystallisation from hot water. Yield, 0·3 grm.

Alanyl glucosamine anhydride when heated quickly turns pale brown at 245–250° and melts at 269–272°, yielding a black liquid. It is moderately soluble in cold and readily soluble in hot water, but it is almost insoluble in cold and only sparingly soluble in hot absolute alcohol. On prolonged heating, the aqueous solution of alanyl glucosamine anhydride slowly reduces Fehling's solution, yielding red copper oxide, or ammonio-silver nitrate solution, giving a silver mirror; but when an aqueous solution of the anhydride is shaken and warmed for two hours with a little more than one molecular proportion of either phenyl hydrazine dissolved in dilute acetic acid, or semicarbazide hydrochloride dissolved in excess of sodium acetate solution, no phenyl hydrazone or semicarbazone is formed, and the resulting solutions on evaporation to crystallisation under reduced pressure yield most of the original anhydride unaltered. As a primary amine, the anhydride is readily soluble in dilute or concentrated hydrochloric acid, and when heated with alcoholic potash and chloroform yields an unpleasant carbylamine odour; but when an aqueous solution of the anhydride is mixed with an aqueous solution of picric acid and afterwards evaporated to crystallisation under reduced pressure no picrate is formed and most of the original anhydride crystallises out unchanged.

0·1194 gave 0·2041 CO_2 and 0·0694 H_2O. C = 46·61; H = 6·50.
0·1322 „ 13·8 c.c. N_2 at 14·2° C. and 752 mm. N = 12·27.
$C_9H_{16}O_5N_2$ requires C = 46·51; H = 6·94; N = 12·07 per cent.

α-Bromoisohexoyl Glucosamine, $CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot NH \cdot C_6H_{11}O_5$.

Four grammes of glucosamine hydrochloride (1 mol.) dissolved in 18·6 c.c. of N sodium hydroxide (1 mol.), when treated with 4·8 grm. of α-bromoisohexoyl bromide (1 mol.) and 18·6 c.c. of N sodium hydroxide (1 mol.) in the same way as previously described for α-bromopropionyl glucosamine, and afterwards acidified with hydrochloric acid, yield 6·5 grm. of α-bromoisohexoyl glucosamine. The product crystallises from absolute alcohol in colourless rhombic plates melting and decomposing when heated quickly at 178–181°, and crystallises from water in colourless prismatic needles, melting when heated quickly at 192–195°, yielding a black liquid. The crystals are slightly soluble in cold, and readily so in hot, water or alcohol, either of these liquids being suitable solvents for purifying the solid by crystallisation. They are insoluble in ether, but dissolve slowly in cold ammonia or alkali hydroxides, yielding yellow solutions. The warm aqueous solution of α-bromoisohexoyl glucosamine readily reduces alkaline copper solutions, yielding red copper oxide, or ammonio-silver nitrate solution, giving a silver mirror; but, like α-bromopropionyl glucosamine, does not appear to react with either phenyl hydrazine or semicarbazide.

0·6189 gave 21·0 c.c. N_2 at 13·8° C. and 746 mm. N = 3·96.

0·2240 „ 0·1175 AgBr. Br = 22·33.

$C_{12}H_{22}O_6NBr$ requires N = 3·93; Br = 22·45 per cent.

Leucyl Glucosamine Anhydride, $C_{12}H_{22}O_5N_2$.

One gramme of α-bromoisohexoyl glucosamine, when treated with concentrated aqueous ammonia in the same way as described for α-bromopropionyl glucosamine, yields 0·25 grm. of leucyl glucosamine anhydride, which crystallises from water in colourless prismatic needles. When quickly heated, it sinters about 205° and melts at 213–215°, yielding a brownish black liquid. It is moderately soluble in cold, and readily soluble in hot, water, but it is difficultly soluble in cold, and only slightly soluble in hot, absolute alcohol. On prolonged heating, the aqueous solution of leucyl glucosamine anhydride slowly reduces Fehling's solution, yielding red cuprous oxide, or ammonio-silver nitrate solution, giving a silver mirror, but, like alanyl glucosamine anhydride, does not appear to react with either phenyl hydrazine or semicarbazide. The anhydride is readily soluble in dilute or concentrated hydrochloric acid, and, when heated with alcoholic potash and chloroform,

yields an obnoxious carbylamine odour, but, like alanyl glucosamine anhydride, does not appear to unite with picric acid.

0·2193 gave 0·4217 CO_2 and 0·1492 H_2O. C = 52·44; H = 7·62.
0·1905 „ 16·0 c.c. N_2 at 13·8° C. and 761 mm. N = 10·01.
$C_{12}H_{22}O_5N_2$ requires C = 52·52; H = 8·09; N = 10·22 per cent.

α-Bromolauryl Glucosamine, $C_{11}H_{22}Br{\cdot}CO{\cdot}NH{\cdot}C_6H_{11}O_5$.

Four grammes of glucosamine hydrochloride (1 mol.) dissolved in 18·6 c.c. of N sodium hydroxide (1 mol.), when treated with 5·6 grm. of α-bromolauryl chloride (1 mol.) and 18·6 c.c. of N sodium hydroxide (1 mol.) in the same way as previously described for α-bromopropionyl glucosamine, and afterwards acidified with hydrochloric acid, yields 7·6 grm. of α-bromolauryl glucosamine. The product crystallises from hot absolute alcohol in colourless rhombic plates, which, when heated quickly, turn brown at 183–186°, and melt with frothing at 194–196°, yielding a dark brown liquid. The crystals are insoluble in hot or cold water, but moderately soluble in hot absolute alcohol. They are insoluble in ether and almost insoluble in concentrated ammonium hydroxide, but they dissolve in hot solutions of sodium or potassium hydroxide, with evolution of ammonia and formation of brown solutions. The crystals are insoluble in dilute hydrochloric acid, and only slightly soluble in hot concentrated hydrochloric acid, showing that the amino-group, and not the hydroxyl groups of glucosamine, has been attacked during the condensation. Like the other α-bromoacyl glucosamines, it readily reduces hot alkaline copper solutions, yielding red cuprous oxide, or ammonio-silver nitrate solution, giving a silver mirror.

0·5855 gave 16·8 c.c. N_2 at 12·0° C. and 747 mm. N = 3·38.
0·2055 „ 0·0885 AgBr. Br = 18·32.
$C_{18}H_{34}O_6NBr$ requires N = 3·18; Br = 18·15 per cent.

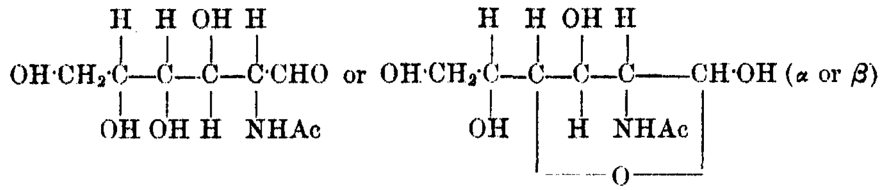
α-Aminolauryl Glucosamine Anhydride, $C_{18}H_{34}O_5N_2$.

Owing to the insolubility of α-bromolauryl glucosamine in ether or in aqueous ammonia, the preparation of the anhydride of α-aminolauryl glucosamine is a process of considerable difficulty. One gramme of α-bromolauryl glucosamine and 500 c.c. of concentrated aqueous ammonia when shaken for 14 days at ordinary temperatures, or allowed to stand for one year at ordinary temperatures, or heated for four hours at 100° C. in a pressure bottle, yield a soapy emulsion, but only a very small quantity of the bromide goes into solution, and almost all of it is recovered unchanged on filtration. The brown ammoniacal solutions on evaporation to dryness under reduced pressure left small brown residues, which on being washed with absolute

alcohol yielded colourless crystals, but too small in quantity to establish their composition and properties, though obviously the anhydride of α-amino-lauryl glucosamine.

Constitution of the α-Bromoacyl Glucosamines and the Anhydrides of α-Aminoacyl Glucosamines.

The analyses and properties of the α-bromoacyl glucosamines are in strict accordance with their representation by aldehydic or glucosidic formulæ similar to those generally adopted for glucosamine,* viz.:—



where Ac is a bromoacyl group of elements.

The representation of the anhydrides of α-aminoacyl glucosamines by constitutional formulæ is, however, a more difficult matter, inasmuch as no satisfactory explanation has yet been given of the much simpler anhydrides formed by the action of ammonia or alkalies on glucose and its derivatives.† It is a matter of conjecture to state from what part of the molecules the elements of water are abstracted when the α-bromoacyl glucosamines react with aqueous ammonia. The feebly basic and slightly reducing properties of the anhydrides of α-aminoacyl glucosamines may be explained by assuming that the elements of water are withdrawn between the amino- and the aldehydic groups with the consequent formation of a linkage between them, which linkage is only broken by the prolonged action of hot alkaline copper solutions. But, on the other hand, as the elements of water seem to disappear so often when glucose and its derivatives react with ammonia or alkalies, it is more probable that when a molecule of an α-bromoacyl glucosamine interacts with aqueous ammonia a molecule of water is abstracted from the glucose portion of the molecule in much the same way as in other anhydro-derivatives of glucose. We mean to continue further this investigation.

In conclusion we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed the greater part of the cost of this investigation.

* *Cf.* J. C. Irvine and A. Hynd, 'Trans. Chem. Soc.,' 1912, vol. 101, p. 1128.

† *Cf.* J. C. Irvine, R. F. Thomson, and C. S. Garrett, 'Trans. Chem. Soc.,' 1913, vol. 103, pp. 238–249; E. Fischer and K. Zack, 'Ber.,' 1912, vol. 45, pp. 456–465, 2068–2074.

The Transition from the Elastic to the Plastic State in Mild Steel.

By A. ROBERTSON, M.Sc., and G. COOK, M.Sc.

(Communicated by Prof. J. E. Petavel, F.R.S. Received April 9,—Read June 19, 1913.)

In the ordinary testing of mild steel the yield point is indicated by the sudden extension of the specimen and the accompanying drop of the beam of the testing machine which occur at this point. This fact would suggest that some reduction of the stress in the specimen under test takes place, and autographic records of tests furnish evidence of the existence of a region immediately after yield in which the relation of stress to strain is of a complicated nature, and in which the intensity of the stress is less than that which caused the yield. It has been shown by Sir Alfred Ewing and Dr. Rosenhain* that the yield phenomenon is due to the formation of planes of cleavage in the crystals, along which sliding takes place. The fact that a greater stress is required to initiate the sliding movement than to maintain it has a direct bearing upon the stress distribution on surfaces subjected to non-uniform stresses when yield in any part takes place, and the object of the experiments here described was to determine the minimum stress in mild steel during the transition from the elastic to the plastic state.

In the usual methods of obtaining autographic records the effect is considerably obscured by the inertia of the loading appliances, and the impossibility of limiting the extension to the degree required, so that the relation of the recorded load to the strain in the region under consideration is, in these circumstances, to a great extent fictitious. Sir Alexander B. W. Kennedy,† some 27 years ago, described a method whereby inertia effects were eliminated, and obtained, as a result, a reduction of stress immediately after yield of about 16 per cent. Since the experiments here described by the present writers were carried out, Prof. W. E. Dalby has published an account‡ of an optical autographic recorder, in which the measurement of the load is effected in a manner similar to that adopted by Kennedy, and in tests carried out on mild steel has observed a reduction of stress of about 13 per cent.

* 'Roy. Soc. Proc.,' vol. 65, p. 172.

† 'Proc. Inst. Mech. Eng.,' 1886.

‡ 'Roy. Soc. Proc.,' vol. 86, p. 414.

In neither of these cases were any special precautions (other than the use of spherical seatings) taken to ensure that the stress distribution across the section of the test specimen was uniform; such precautions are, indeed, unnecessary when it is desired merely to obtain a record of the load-strain relation throughout the plastic stage. Prof. C. A. M. Smith has pointed out,* however, the importance of securing concentric loading of the specimen (and consequent uniformity of stress) in experiments dealing with the determination of the elastic limit and yield point, and has shown that even when the specimen is supported by nuts resting on spherical seatings, such a condition is not necessarily guaranteed.

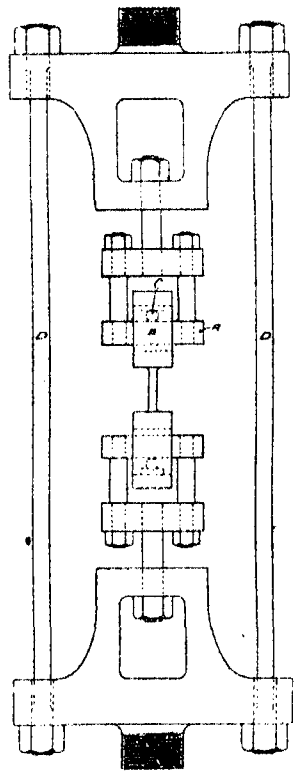


FIG. 1.

An arrangement whereby a much closer approach to truly axial loading is secured has been described by the authors in a previous paper,† and has been used in the present work. By this means, and also by limiting the extension of the specimen immediately after yield to a very small amount, the authors have observed at this point a reduction of stress greater than 23 per cent. in 11 specimens of mild steel.

A sketch of the complete apparatus is shown in fig. 1. The specimen, of carefully annealed mild steel machined to about $\frac{3}{8}$ inch diameter, was screwed at each end into a hollow rectangular block of steel to which the load was transmitted through a steel ball co-axial with the centre line of the specimen and resting on the hardened surface of a stout steel cross-bar A. Care was taken in machining the block B to ensure that the centre line of the hole into which the specimen was tightly screwed passed through the centre of the spherical cavity C resting upon the steel ball. The whole was attached to two heavy castings machined to fit the testing machine grips. Two bars of mild steel $\frac{3}{4}$ inch diameter were supported by nuts bearing on machined surfaces at each side of the casting, and extensometers attached to them, by means of which the load occurring at any time in them was determinable, both bars having previously been independently calibrated. The manner of carrying out a test was as follows:—

* 'Engineering,' Dec. 10, 1909, vol. 88, p. 796.

† 'Engineering,' vol. 92, p. 786.

An initial load of one ton was applied to the test specimen (corresponding to a stress of 8 tons per square inch) before the nuts supporting the side bars D were tightened, the zero readings of the extensometers having been first observed. The load on the whole apparatus measured on the beam of the testing machine was then increased by small amounts, and the share taken by the side bars calculated from the extensometer readings after each increment, thereby obtaining by difference the load on the specimen. Yield occurred in the latter while there was still a large margin of elasticity left in the side bars D, and the increased load taken up by these at the moment of yield was a measure of the reduction of load in the specimen. The beam of the testing machine remained perfectly steady throughout the process, and deformation in the test piece was prevented except to the extent of the change of elastic deformation of the side bars and axial loading shackles.

The results of the tests are tabulated below. The stress in the specimen immediately before and after yield and the percentage reduction are given in the last three columns. It will be seen that in one test the latter attained a value as high as 36 per cent., whilst in the remainder, with one exception, the values ranged between 24 and 30 per cent.

Number of specimen.	Diameter.	Length.	Stress before yield.	Stress after yield.	Percentage reduction of stress.
	in.	in.			
1	0·387	2·00	17·1	10·9	36
2	0·399	2·00	16·6	12·7	24
3	0·376	2·00	18·3	13·3	27
4	0·389	2·00	17·9	12·9	28
5	0·378	2·00	18·4	12·8	30
6	0·384	2·00	18·5	13·5	27
7	0·389	2·00	19·4	12·6	35
8	0·383	2·00	15·1	11·3	25
9	0·401	1·11	16·5	12·0	27
10	0·363	0·93	18·1	15·1	17
11	0·407	0·80	16·9	12·3	27
12	0·398	0·50	17·1	13·0	24

The specimens were made from ordinary mild steel, and the variations in the results of the tests may be due to a number of causes, of which the chief are (1) slight differences in composition or annealing, (2) slight deviations from true axiality in the applied load. It may be mentioned here that a deviation of one five-hundredth of an inch of the resultant load from the axis of the specimen would cause the stress on one side of the specimen to be 4 per cent. in excess of the mean (measured) stress, and the

observed stress at yield might therefore be below the true yield stress by an amount which would considerably affect the value of the stress reduction. A confirmation of the results arrived at is, however, obtained by experiments on bending and torsion to be described later.

In the course of the experiments it was considered desirable to determine the actual extensions in the test specimen immediately after yield in order to construct a stress-strain diagram. The short length of the specimen, however, prevented the use of any of the laboratory extensometers. A special apparatus was constructed for the purpose, the principle of which was that of Marten's extensometer. The diagram shown in fig. 2 has been constructed from observations taken with this instrument on specimen

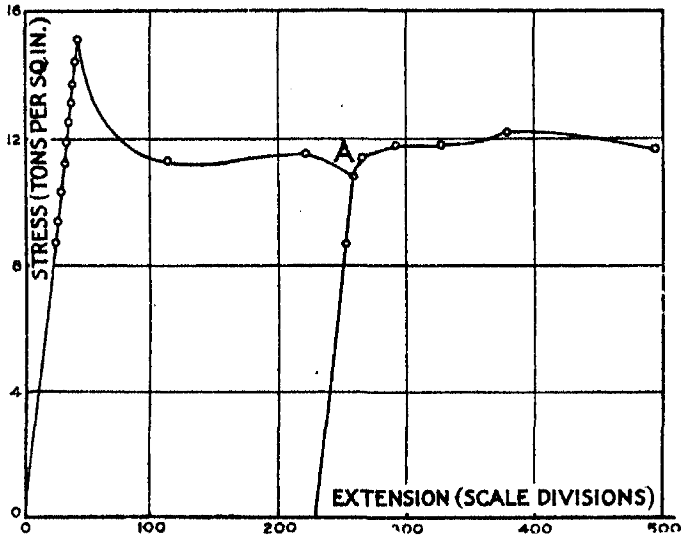


FIG. 2.

No. 8. The point A is the limit beyond which it was impossible to carry the extension without readjustment of the apparatus, on account of the necessity of keeping the stress in the side bars well below the elastic limit. At this point the load was therefore relieved, the necessary adjustment made, and a second test performed of the same specimen. It will be seen that the stress now required to cause further deformation is not appreciably different from that existing in the specimen at the conclusion of the previous test. It would appear, therefore, that the "drop" is a phenomenon associated solely with the breakdown from the initial elastic state, and that the reduced stress remains at a fairly constant value over a total strain equal to several times the magnitude of the elastic strain.

Further evidence in confirmation of the results arrived at in the above

manner for the magnitude of the stress reduction was sought in the behaviour of the steel when subjected to non-uniform stress. The cases of bending and torsion furnish two examples of such a stress distribution. In these cases, by making certain assumptions, an equation can be obtained expressing the relation between the moment, displacement, and stress reduction after yield has taken place. The magnitude of the reduction may therefore be obtained from the experimental observation of the moment and displacement.

Consider first the case of a bar of rectangular section subjected to a uniform bending moment. If the stress at every point is below the elastic limit, its magnitude is proportional to the distance from the neutral plane, and is therefore a maximum at the extreme surfaces. The displacement δ at the middle point is given by

$$\delta = \frac{fl^2}{4\mathrm{E}d},$$

where $f =$ stress at outer fibres, $l =$ length, $d =$ depth, $\mathrm{E} =$ Young's modulus.

When the bending moment is increased beyond a certain amount, yield occurs in those parts subjected to the greatest stress, namely, the outer fibres. It will be assumed :—

(1) That plane sections remain plane.

(2) That the stress in the overstrained part is uniform. This assumption is allowable, in view of the fact that the total strain in those parts is comparable to the elastic strain, and the stress variation has been shown to be very small for extensions of this magnitude (see fig. 2).

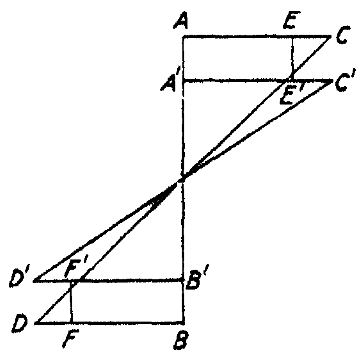


Fig. 3.

(3) That the greatest stress in parts still elastic is equal to that required to initiate the yield.

(4) That the stress distribution is symmetrical about the neutral plane.*

Let AB (fig. 3) represent the normal section of the beam, and f be the maximum direct tensile stress the material is capable of withstanding without overstrain. If AC = BD = f to some scale, the stress at any point in AB, when the

* This involves the assumption that the stresses at yield and the reduction of stresses after yield are the same in tension and compression. If these two values are different, the reduction of stress actually occurring on the tension or compression sides must be greater than the estimate deduced from the following analysis.

maximum bending moment M consistent with perfect elasticity in all parts is applied, will be given by the ordinate at that point to the line CD.

If the bending moment is increased to some value M′, the extreme fibres will be overstrained, and the beam may be considered as made up of two parts, (1) a central elastic portion of depth d' in which the maximum stress will still be f, and (2) two portions, one at the upper and one at the lower surface, in which the stress is assumed uniform, and in magnitude equal to xf. The new distribution may be represented diagrammatically by the lines EE′C′D′F′F (see fig. 3). The displacement δ' produced by M′ may be obtained by considering the equilibrium of the central elastic portion, and is given by

$$\delta' = \frac{fl^2}{4\mathrm{E}d'}.$$

But δ, the maximum displacement when the whole of the beam is elastic is given by

$$\delta = \frac{fl^2}{4\mathrm{E}d},$$

and, therefore,

$$\frac{d'}{d} = \frac{\delta}{\delta'}.$$

Now M′ is equal to the sum of the moments of resistance of the different parts of the beam. Hence

$$\mathrm{M}' = \frac{fbd'^2}{6} + \frac{xfb}{4}(d^2 - d'^2) = \mathrm{M}\frac{d'^2}{d^2} + \frac{xfbd^2}{4}\left(1 - \frac{\delta^2}{\delta'^2}\right)$$
$$= \mathrm{M}\left(\frac{\delta}{\delta'}\right)^2 + \frac{3x}{2}\mathrm{M}\left\{1 - \left(\frac{\delta}{\delta'}\right)^2\right\}.$$

A number of tests were made on bars of annealed mild steel machined accurately to a rectangular section about $\frac{3}{8}$ inch deep and $\frac{3}{16}$ inch wide. A uniform bending moment was secured by applying the load outside the supports which were 3 inches apart. The displacement of the central point relative to two fixed points situated in the neutral plane over the supports was obtained by observing the rotation of a mirror attached to a tripod resting with one leg on the beam and the other two on supports rigidly connected to the two points of reference. The load was applied gradually, and the displacement read after each addition. While the whole of the bar was elastic the position of equilibrium was reached immediately. When yield occurred, the displacement continued to increase for a short time without the application of further load.

A diagram is given in fig. 4 showing the relation of bending moment to displacement throughout the test. The relation, as will be seen, is a linear one until yield takes place, the latter being very definitely located by the

change from the straight line to a somewhat irregular curve. The series of curves shown by dotted lines represent the theoretical relation between bending moment and displacement for different values of the stress reduction, as given by equation (1).

It may be noted that a reduction of 33·3 per cent., corresponding to a value of $x = \frac{2}{3}$, would be represented by a horizontal line, the displacement

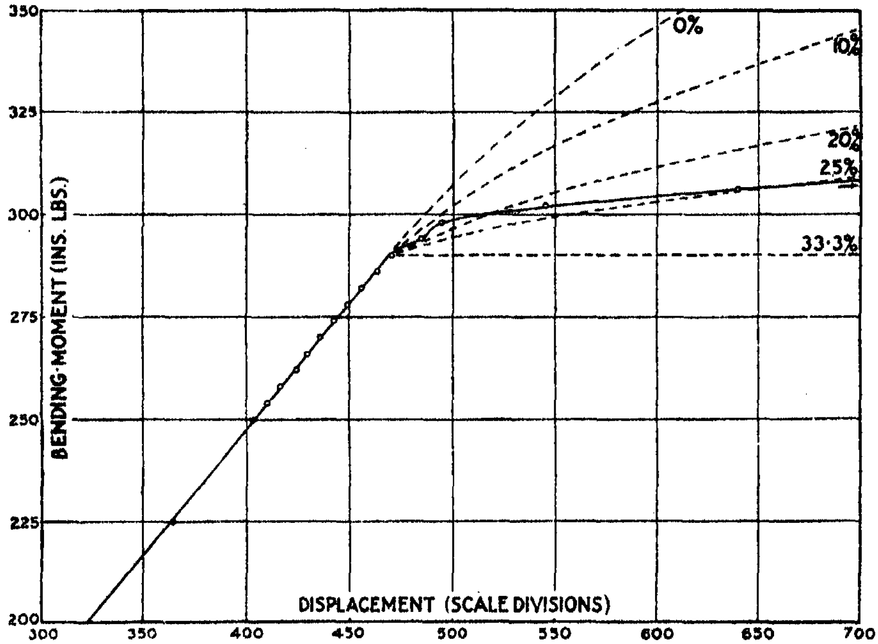


Fig. 4.

increasing without the application of additional load until the true plastic condition was reached in the outer fibres.

It will be seen that the experimental curve, in the earlier stages after yield, lies in the region between the theoretical curves for 10 per cent. and 20 per cent. reduction. Subsequently, however, it takes up a position corresponding to a stress reduction of about 25 per cent. The irregularity of the course followed by the curve may be ascribed to two causes, namely :—

(1) The probability that yield does not occur over the whole length of the bar at the same time, but is at first localised at some point, from which it extends gradually, producing the slow continuous increase in the displacement under constant load.

(2) The probability that yield in tension and compression do not occur simultaneously.

Both these effects would make the displacement less than if yield took place simultaneously over the whole of the tension and compression surfaces. Therefore it is probable that the position of the curve in the earlier stages of yield does not correspond with the true value of the stress reduction, and that the comparison of the theoretical and experimental curves is more legitimate in the later stages when yield has probably taken effect over the whole length. Thus, in fig. 4, although the double bend following on the yield point might correspond to a difference in the yield stress in tension and compression, it cannot be regarded as conclusive evidence on this point. Though no definite value for the magnitude of the stress reduction can be looked for from the bending experiments, they suggest limits between which it may lie. These limits would appear to be 25 and 33 per cent.

The yield phenomenon in ductile materials is probably due mainly to shearing stress,* and therefore it was expected that some definite information on the value of the stress reduction at yield would be obtained from the consideration of a round bar subjected to torsion. In this case the stress on every normal section is one of pure shear and varies uniformly from zero at the axis to a maximum at the surface, provided that the elastic limit is not exceeded. An analytical investigation carried out in a precisely similar manner to that of a beam leads to the equation

$$M' = M\left(\frac{\theta}{\theta'}\right)^3 + \frac{4x}{3}M\left\{1-\left(\frac{\theta}{\theta'}\right)^3\right\},$$

where M and M′ are twisting moments, and θ and θ' the corresponding angular displacements at and after yield.

It will be seen from this equation that if x is less than $\frac{3}{4}$, or, in other words, if the stress reduction is greater than 25 per cent., the angular displacement when the yield point is reached will continue to increase without further increment in the twisting moment until the true plastic state is reached.

In experiments carried out on annealed mild steel bars $\frac{1}{2}$ inch diameter, it was found that this actually took place. When the yield point was reached, the angular displacement increased at a slow but uniform rate under the same torque. The machine in which the experiment was carried out only permitted a limited angular displacement, and when this was reached, the displacement was still increasing. A diagram showing the experimental relation between twisting moment and angular displacement, together with the theoretical curves for various values of the percentage reduction is given in fig. 5.

* J. J. Guest, "The Strength of Ductile Materials under Combined Stress," 'Phil. Mag.,' July, 1900, Series V, vol. 50.

The torsion tests would therefore suggest that the reduction in stress is probably greater than 25 per cent.

The results of the tests in direct tension, bending, and torsion would appear to fix the stress reduction which occurs at the yield point in mild steel at a value much greater than has hitherto been suspected.

These experiments also suggest an explanation of an unexpected phenomenon observed by the present writers during some tests carried out to determine the pressure necessary to cause yield on the inner surface of thick hollow mild steel cylinders. The extension of the outer diameter was measured by a

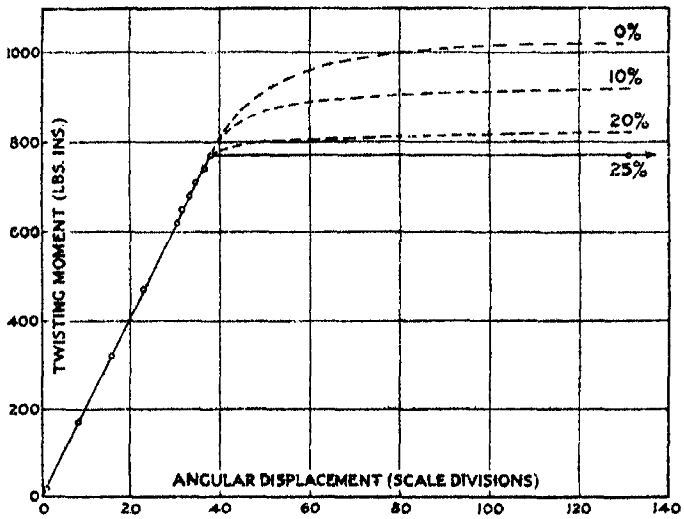


FIG. 5.

special extensometer, as the internal pressure was increased, and in some cases, when yield took place, a retrogression in the pressure-strain curve occurred, the diameter to which the extensometer was fixed contracting instead of extending.* On subsequently cutting the cylinder it was found that the hole was quite central, and that, therefore, the phenomenon was not due to eccentricity. An explanation may be given in the following manner. Owing to lack of homogeneity, yield may first take place on one side of the hole. The stress at that part may thereby be relieved to the extent of about 25 per cent., and the effect upon the rest of the cylinder will be the same as if the hole were elliptical. If the deformation of the external surface were measured on the diameter passing through the centre of the yielded part, a

* A similar effect has been observed by Mr. L. B. Turner, see 'Engineering,' vol. 92, p. 117.

contraction would probably be observed, which would not be converted into an extension until the whole of the internal surface had yielded.

The authors desire to place on record their indebtedness to Prof. J. E. Petavel, F.R.S., for many valuable suggestions in the course of this work.

The Attainment of High Potentials by the Use of Radium.

By H. G. J. Moseley, B.A., John Harling Fellow, University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received April 22,—Read May 1, 1913.)

The original aim of the work described in this note was to measure the energy and numerical importance of each of the many distinct kinds of β-particles emitted by a single radioactive substance. Calculation of the energy of a β-particle from observation of its deflection in a magnetic field* involves assumptions which are as yet insufficiently supported by experiment. Theoretically both the energies and distribution of the particles could be directly measured by giving a gradually increasing positive charge to the source of radiation; for, when the potential of the source is $+V$, electrons possessing energy less than eV will be drawn back to the source of radiation. Unfortunately, more than a million volts would be necessary to stop the fastest β-particles, and no method is at present known of maintaining such a high potential *in vacuo*. It was thought that this difficulty might possibly be overcome by using the active material itself in order to produce the high potential according to the principle employed in Strutt's radium clock.† If the source of radiation were perfectly insulated its potential would rise until the swiftest β-particles could no longer escape. The present note deals with experiments‡ made to test whether this method were practicable. It was found that high potentials were readily obtained, but the attempt to attain to a million volts failed through the difficulties of insulation encountered. But few experiments were completed, and many failed as the result of accident. This shows that, even if perseverance had been rewarded by greater success, technical difficulties, accentuated by

* Planck, 'Phys. Zeit.,' 1906, vol. 7, p. 753.

† Strutt, 'Phil. Mag.,' 1903, vol. 6, p. 588.

‡ A preliminary account of these experiments was communicated to the Manchester Literary and Philosophical Society, November 12, 1912.

every effort to improve the insulation, would probably have prevented the practical application of the method. It seemed, therefore, useless to pursue the matter further, until more is known of the reasons why the insulation of a vacuum breaks down.

In these experiments the source of β-radiation was 20 millicuries or more of purified radium emanation contained in a thin bulb—marked B in fig. 1—

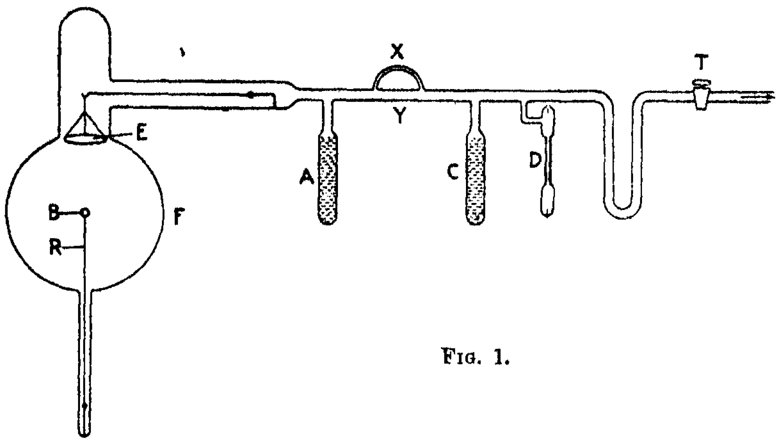


FIG. 1.

of about 1 cm. diameter. The bulb, which was just thick enough to stop all α-radiation, was supported by a fine silica rod R inside an exhausted glass flask F of 1 litre capacity. The rod, of diameter about 0·8 mm., was freshly drawn from transparent fused silica. The surface of the bulb and the flask was coated with silver, which was found to retain a trace of conductivity when subsequently heated to 400° C., though it then became almost transparent. The potential gained by the bulb was measured by a simple form of attracted disc electrometer, a circular aluminium disc being hung from the arm of a horizontal silica spring, the other end of which was soldered with aluminium to a projection from one of the glass walls of the flask. By observing with a microscope the displacement of the disc, the force of attraction exerted on it by the bulb was measured, and from this it was easy to calculate the charge and the potential acquired by the bulb. The force of a dyne displaced the spring by about 0·1 mm. The disc was hung just at the entrance to the mouth of the flask, so that the remainder of the flask wall served the purpose of a guard-ring.

In order to diminish the risk of discharge through any trace of gas left in the vessel, the greatest care was taken in the exhaustion of the flask. Instead of an attempt being made to measure the residual pressure in the apparatus, methods of exhaustion were followed which, in the hands of

others, have yielded the highest attainable vacua.* To remove water and other volatile substances the entire apparatus was subjected to prolonged heating at 400° C., and exhausted by a Gaede mercury pump. Everything was heated electrically, the main flask F being surrounded by a cylinder of sheet asbestos wound with nickel wire and insulated with kieselguhr, while the charcoal bulbs A and C and the connecting tubes were enclosed in small tube furnaces. At first, almost as soon as pumping ceased, the hydrogen and carbon monoxide lines appeared in the discharge tube D, which was used to test the degree of exhaustion. After some hours' heating, and after repeatedly filling the whole system with dried nitrogen and then re-exhausting, a few minutes' pumping sufficed to prevent the passage of a discharge in D, and this condition was then maintained for an hour or more after pumping had ceased. To obtain this result it was necessary to employ a U-tube cooled in liquid air to condense the vapours of mercury and tap-grease, and the charcoal in A and C, which was being heated all the time, had to be properly prepared. The preparation, which followed the directions given by Hupka,† consisted chiefly in heating freshly-made coconut charcoal to 450° *in vacuo*, until gas was no longer evolved; a tedious process, since the hydrocarbons are very slowly volatilised and decomposed. Before the final exhaustion the wide by-pass Y was sealed off. Then after five hours' pumping the tap T was closed, and C cooled in liquid air. After a further five hours the apparatus was sealed off at X, and quickly removed from the furnaces. A was then kept in liquid air during the course of an experiment. If all went well the exhaustion was completed in about 24 hours.

As soon as the apparatus had had time to cool, it was seen that the bulb was abruptly discharged every few minutes. The disc of the electrometer was first displaced by an amount which showed that the bulb was very highly charged, and then suddenly flew back to its original position, while in a dark room a yellowish-green flash was seen to light up the bulb, the rest of the interior of the flask remaining dark. The displacement of the disc immediately recommenced, at first slowly, since the force of attraction depended on the square of the attracting charge, then at an ever increasing rate, until the maximum was approached. The disc then began to move more slowly, at times it would falter or fall back a little, as if some slight discharge were taking place. Finally, without warning, came the complete discharge, the time occupied by the cycle being erratic, but

* Heuse and Scheele, 'Zeitschr. f. Instrumentenk.,' 1909, vol. 29, p. 46; Poynting and Barlow, 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 534.

† Hupka, 'Ann. d. Physik,' 1910, vol. 31, p. 169.

corresponding roughly with the interval expected having regard to the quantity of active material and the capacity of the system. The thin disc, if not in metallic connection with the flask, gained a free positive charge, which pulled it back towards the neighbouring silvered surface; a difficulty easily overcome by occasionally tilting the apparatus slightly. The bulb could be discharged at will by directing on to the apparatus a powerful beam of X-rays, the necessary charge being doubtless carried to the bulb by the swarm of electrons released from the surface of the flask.

A preliminary experiment made with simpler apparatus showed that a potential of the order of 150,000 volts could readily be obtained. In the first successful attempt to use the apparatus described above, the bulb, of diameter 9 mm., was made of quartz. As soon as the apparatus was completely exhausted a spark perforated the bulb and the radium emanation began to diffuse out and condense on the cooled charcoal. It was several days before the greater part of the emanation had been transferred, so that the size of the hole, calculated* from the rate of effusion, must have been only of the order of 10^{-4} mm. This accident appeared not to affect the discharge potential, which was found to be $1{\cdot}5 \times 10^5$ volts, and remained the same even when most of the emanation had left the bulb. The experiment was repeated with a glass bulb of 1 cm. diameter through which a platinum wire was sealed, in order to prevent the passage of a spark through the glass. The tip of the bulb was fixed by the wire into a small silica tube fused on to the silica rod. The maximum discharge potential observed was $1{\cdot}7 \times 10^5$ volts, but this figure was probably slightly over-estimated, since the silica tube if charged would itself have attracted the disc appreciably. In each case the discharge potential decreased as soon as the charcoal was heated to room temperature, but was still of the order of 10^5 volts. This decrease is a strong indication that the sudden discharge, which always limited the potential, took place through the residual gas and not along the silica rod. The slow and irregular rate of charging at high potentials may have been due in part to conduction along the silica. The number of particles escaping must also have been somewhat diminished, since 160,000 volts will turn back any particle emitted with velocity less than 0·65 that of light.

Study of the experimental circumstances of discharge in high vacua has been singularly neglected. The only systematic work on the subject is that of Madelung.† This author, working with parallel electrodes at distances up to 0·4 mm., concluded that in the highest vacua a discharge takes place as

* Knudsen, 'Ann. d. Physik,' 1909, vol. 28, p. 999.

‡ Madelung, 'Phys. Zeit.,' 1907, vol. 8, p. 68.

soon as the electric force at the surface of the electrodes exceeds 3 or 4×10^5 volts per centimetre. The highest potential used by him was only about 12,000 volts, but his results showed clearly that under his conditions the discharge could not be explained by the ordinary theory of ionisation by collision in gases. In the present experiments there can be no doubt that the process of exhaustion was really effective, as special tests were made to guard against the possibility of mistake. The residual pressure was therefore so small that ordinary ionisation by collision was out of the question.

When a bulb of 9 mm. diameter is charged to a potential of $1 \cdot 5 \times 10^5$ volts, the electric force at the surface is $3 \cdot 3 \times 10^5$ volts per cm., and the agreement between this figure and that found by Madelung may well be more than a coincidence. Again, in the one experiment the tip of a platinum wire projected from the glass bulb, and the failure of this point, at which the electric force must have been enormous, to promote discharge is paralleled by Madelung's observation that the discharge potential was much higher between pointed electrodes than between parallel plates at the same distance. The nature of this discharge at very low pressures is still obscure, but it is probably essentially the same as the discharge found by many observers to pass in air at less than the minimum spark potential between electrodes very close together. This latter discharge has been the cause of much controversy; partly because some observers have looked for a visible spark, while others have been content with the passage of a minute current; partly on account of experimental difficulties introduced by the use of air and consequent restriction to minute spark-gaps; and partly because the discharge seems to be much influenced by the nature and condition of the electrodes. With varying length of spark-gap the discharge takes place when the electric force at the electrodes reaches a fixed limiting value, which is apparently uninfluenced by the presence of any kind of gas.* Various observers† using different electrodes have found values ranging from rather more than 10^6 up to 10^7 volts per centimetre, while Almy‡ obtained no visible discharge with an electric force of nearly 2×10^7 volts per centimetre. It is not clear why the maximum electric force found by Madelung and in the present experiments should be so much lower, but very possibly the area of the electrode surface is here a factor of importance.

For these reasons it was hoped that the discharge might be prevented by

* Hobbs, 'Phil. Mag.,' 1905, vol. 10, p. 617; G. Hoffmann, 'Phys. Zeit.,' 1910, vol. 11, p. 961.

† Hobbs, *loc. cit.*; G. Hoffmann, *loc. cit.*; Earhart, 'Phil. Mag.,' 1901, vol. 1, p. 147; Shaw, 'Roy. Soc. Proc.,' 1903, vol. 73, p. 337; Kinsley, 'Phil. Mag.,' 1905, vol. 9, p. 692; Rother, 'Phys. Zeit.,' 1911, vol. 12, p. 671.

‡ Almy, 'Phil. Mag.,' 1908, vol. 16, p. 456.

increasing the size of the bulb, and so reducing the surface intensity of electrification. An experiment was, therefore, tried using a bulb of 5 cm. diameter. The electrometer spring was made very much stronger in anticipation of a much greater force of attraction, but otherwise nothing was altered. Mr. Baumbach, the University glass blower, successfully undertook the difficult task of assembling the apparatus. Owing to the increased capacity of the bulb it charged up much more slowly than before. Instead, however, of discharging itself at intervals, it now became charged to an almost constant potential, which it retained, except when artificially discharged by the use of X-rays, for at least three weeks. During that time this potential gradually rose from 10^5 to $1{\cdot}1 \times 10^5$ volts, while the current carried away by the β-particles fell from about 10^{-11} amperes to 2 per cent. of that value, owing to the decay of the radium emanation. The potential was uninfluenced by the temperature of the charcoal bulb, and there can be little doubt that it was limited by a leak along the silica support, which was now stouter and less scrupulously cleaned than before. This curious case of the potential being independent of the current carried by the silica strongly resembles conduction in a gas at a potential just below that required to produce a spark. There variation of the current over wide limits is accompanied by very slight change in the potential, and perhaps the conduction in the silica had a similar origin. In the event of this method of maintaining a constant high potential proving of practical use, much time could probably be saved by cutting short the process of exhaustion.

We see then that a radioactive substance may by the emission of β-radiation charge itself positively to a potential difference of more than 150,000 volts from its surroundings. This fact provides a striking direct proof of the large amount of energy involved in the expulsion of a β-particle. It also extends somewhat our knowledge of the insulating properties of a vacuum. Previously Hupka (*loc. cit.*) had shown that two plates could in a highly exhausted chamber be maintained by means of an influence machine at a potential difference of 90,000 volts, without any discharge taking place. I am indebted to his paper for many useful suggestions.

In conclusion I wish to thank Prof. Rutherford for his kind interest in the progress of this work.

On the Recombination of the Ions Produced by Röntgen Rays in Gases and Vapours.

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1. *Introductory.*

In a space containing both positive and negative ions the concentration of the ions tends to diminish as a result of the union of ions of opposite sign. The number of ions of each sign which disappear in unit time is proportional to the number of collisions between ions of opposite sign. This is proportional to the product of the concentrations of the two kinds of ions and it is customary to express the change in the form of the equation

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}, \tag{1}$$

where n_1 and n_2 are the numbers of positive and negative ions respectively in unit volume, and α is a constant for a gas at a given temperature and pressure; α is called the coefficient of recombination of the ions.

When the concentrations of the two kinds of ions are equal the equation takes the simple form

$$\frac{dn}{dt} = -\alpha n^2,$$

the solution of which is

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t, \tag{2}$$

n_0 being the concentration of the ions initially, and n the concentration after an interval of time t. In what has been said above the effect of diffusion is supposed to be negligible.

The coefficient of recombination is of fundamental importance in the theory of the ionisation of gases, and an experimental verification of equation (2) serves as a general test of the theory. Methods of measuring the coefficient have been devised by Rutherford,* Townsend,† Langevin,‡ and others, and many determinations have been made by different observers.§ The results obtained present some rather wide divergences, both as regards

* Rutherford, 'Phil. Mag.,' 1897, vol. 44, p. 422.

† Townsend, 'Phil. Trans.,' 1899, vol. 193, p. 129.

‡ Langevin, 'Annales de Chimie et de Physique,' 1903, vol. 28, p. 433.

§ McClung, 'Phil. Mag.,' 1902, vol. 5, p. 283; Hendren, 'Phys. Rev.,' 1905, vol. 21, p. 314; Retschinsky, 'Ann. der Physik,' 1906, 4, vol. 17, p. 518.

the absolute values of the coefficient of recombination at a given pressure, and also as regards the manner in which the coefficient varies when the pressure is changed. Thus McClung found a constant value for α for pressures varying from 0·125 to 3 atmospheres, whereas Langevin, in some experiments on air, found that, for a range of pressures from 760 mm. to 250 mm., α was approximately proportional to the pressure.

In view of these divergences, of the fact that no work had been done on vapours, and of the importance of the subject from a theoretical point of view, it was thought that an investigation of the coefficient of recombination of ions in gases and vapours at different pressures would prove a fruitful subject for research.

The work of Bragg and Plimpton has shown that certain peculiarities occur in the initial stages of recombination. It was the author's aim to measure the coefficient when the initial peculiarities have been dissipated, these being the only conditions under which the coefficient has a simple meaning. In this paper is given an account of the work which has been done on some gases and vapours. The measurements on vapours are still in progress.

2. *Experimental Method.*

The methods devised by Rutherford and used by him, McClung and others, are by far the simplest of those that have been employed for the measurement of the coefficient of recombination. However, they serve to verify the law of recombination only in the simple case in which the concentrations of the positive and negative ions are equal. Moreover, in practice, they are subject to certain difficulties. In the first place, the source of ionisation (Röntgen rays in this case) must act for some time, and it is assumed that the source remains of constant intensity. This condition is one which it is notoriously difficult to satisfy, especially in the case of a bulb giving out penetrating rays. In consequence of this the values are liable to present wide divergences, and there is some difficulty in weighing up the results. In the second place, the distribution of the ionisation in the vessel is of no small importance. On account of the secondary radiation which is always present in these experiments, and which may produce intense local ionisation, it is impossible to know in an exact manner the distribution of the ionisation in the vessel. Finally, the effects of the diffusion of the ions to the walls of the vessel are important, and there is some difficulty in correcting for this effect. Langevin* has shown the importance of diffusion in McClung's experiments. At ordinary

* 'Journ. de Physique,' 1905, vol. 4, p. 322.

pressures diffusion accounted for about 10 per cent. of the observed recombination, and, at a pressure of one-eighth of an atmosphere, the values obtained were probably five or six times too large. In Langevin's method these are avoided, and this was the one used throughout these experiments.

Before giving a short account of the method, it may be useful to consider the significance attached by Langevin to the term "number of collisions." Suppose that round each negative ion in an ionised gas a surface is described, the dimensions of which are arbitrary, except that its largest dimension is large compared with the mean free path of an ion, and small compared with average distance between two ions. The number of positive ions which, in a time dt, penetrate into the interior of these surfaces, as a result of the attraction of the negative ions inside, is independent of the dimensions of the surface and of the electric field existing in the gas due to the neighbouring conductors. This number Langevin defines to be the number of collisions between ions of opposite sign in the time dt.

The number of these collisions is given by the expression

$$4\pi (k_1 + k_2)\, n_1 n_2 e\, dt,$$

in which k_1 and k_2 are the mobilities of the positive and negative ions respectively, n_1 and n_2 are the concentrations of the positive and negative ions, and e is the charge on an ion of either sign. This expression contains neither the dimensions of the surface supposed to surround the ion nor the strength of the electric field.

If each collision results in a recombination of the two ions, the rate of change of the concentration of the positive and negative ions will be equal to

$$4\pi (k_1 + k_2)\, n_1 n_2 e.$$

But recombination does not necessarily follow a collision. The initial kinetic energy of the ions, supplemented by the energy due to their mutual attraction, may be so great that the two ions separate again after having approached, or even after having gravitated the one round the other. A fraction ϵ only, necessarily less than unity, of the number of collisions will result in recombination, so that we have

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = -4\pi\epsilon (k_1 + k_2)\, e n_1 n_2.$$

Comparing this with the expression

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = -\alpha n_1 n_2,$$

we have

$$\epsilon = \frac{\alpha}{4\pi (k_1 + k_2)\, e}.$$

In the method described below, this ratio is measured directly under variable conditions. If the laws of recombination and mobilities are exact, the experiment, for a given gas under given conditions of temperature and pressure, ought to furnish for this ratio a constant value, independent of the exterior field and of the intensity of the ionisation. This fraction having been measured and the mobilities of the ions being known, the coefficient of recombination can be deduced.

There remains to be considered the method of measuring this ratio. The principle is as follows:—Suppose we have two parallel plates A and B, and a uniform field in the region between the plates, the direction of the field being from B to A. Let the gas between the plates be ionised by a single flash, of very short duration, from a Röntgen-ray bulb. During the flight of the ions to the two plates there will be a certain number of collisions, and the positive charge which finally reaches the plate A will, for a given initial charge present in the gas, depend on the number of these collisions. Increasing the electric field between the plates decreases the time of flight and therefore the number of collisions, with a consequent increase in the charge on A.

In the case where the total charge Q_0 of either sign, produced in the gas by the single flash of Röntgen rays, is so small that the moving charges do not sensibly modify the field, Langevin has calculated the charge Q received by the plate A and shown that it does not depend on the distribution of the ions between the plates. This quantity is given by the expression

$$\frac{\epsilon Q}{\sigma} = \log_e\left(1+\frac{\epsilon Q_0}{\sigma}\right),$$

in which σ is determined by the relation $X = 4\pi\sigma$, X being the strength of the electric field between the plates. For the proof of this the reader is referred to the original memoir.

Determination of ϵ.—In order to find ϵ, the charges Q_1 and Q_2, received by the plate for different values of the electric field with the same initial ionisation, are measured. If the electric fields are X_1 and X_2, the expressions for Q_1 and Q_2 are

$$\frac{\epsilon Q_1}{\sigma_1} = \log\left(1+\frac{\epsilon Q_0}{\sigma_1}\right) \quad \text{and} \quad \frac{\epsilon Q_2}{\sigma_2} = \log\left(1+\frac{\epsilon Q_0}{\sigma_2}\right), \tag{3}$$

in which $X_1 = 4\pi\sigma_1$ and $X_2 = 4\pi\sigma_2$.

Experiment gives the relative values of the quantities $Q_1, Q_2, \sigma_1, \sigma_2$. Q_1 and Q_2 are proportional to the quantities of electricity received by the electrode in the two cases after one discharge from a Crookes tube, and σ_1 and σ_2 are propor-

tional to the quantities of electricity induced on the electrode at the instant when the electric field is established.

The simplest method of calculating ϵ has been found to be a graphical one, due to Langevin. For convenience of explanation later, it will be convenient to describe this briefly here. Writing

$$x = \frac{\epsilon Q_0}{\sigma_2}, \qquad y = \frac{Q_2}{Q_0},$$

the equations (3) become

$$y = \frac{1}{x}\log(1+x) \quad \text{and} \quad y\frac{Q_1}{Q_2} = \frac{\sigma_1}{x\sigma_2}\log\left(1+\frac{x\sigma_2}{\sigma_1}\right),$$

in which Q_1, Q_2, σ_1 and σ_2 appear only in the ratios Q_2/Q_1 and σ_2/σ_1.

x and y being known, we have

$$\epsilon = xy\frac{\sigma_2}{Q_2}.$$

A curve is now drawn with log x as abscissæ and log y as ordinates, y being given by the relation

$$y = \frac{1}{x}\log(1+x).$$

The points corresponding to x and $x\sigma_2/\sigma_1$ have a known difference of abscissæ

$$\log x - \log\frac{x\sigma_2}{\sigma_1} = \log\frac{\sigma_1}{\sigma_2}.$$

The corresponding ordinates are log y and log yQ_1/Q_2 and their difference is also a known quantity

$$\log y - \log y\frac{Q_2}{Q_1} = \log\frac{Q_1}{Q_2}.$$

In order to determine x and y, it is sufficient to determine on the curve two points P and P′, the abscissæ and ordinates of which differ respectively by the known quantities $\log \sigma_1/\sigma_2$ and $\log Q_1/Q_2$. By moving a transparent paper over the curve it is possible to find these points with both ease and accuracy.

The abscissæ and ordinates of these points are log x and log y, and we have

$$\log\epsilon = \log x + \log y + \log\sigma_2 - \log Q_2.$$

An example will illustrate this. In an experiment on dry carbon dioxide at a pressure of 614 mm. of mercury and a temperature of 13·5° C., the following results were obtained :—

$$\log Q_1 = 2{\cdot}69020, \qquad \log\sigma_1 = 2{\cdot}2954,$$
$$\log Q_1/Q_2 = 0{\cdot}02927, \qquad \log\sigma_1/\sigma_2 = 0{\cdot}3945.$$

The values of x and y obtained from the curve were

$$\log x = \bar{1}\cdot 400, \qquad \log y = 1\cdot 950.$$

Hence $\log \epsilon = \bar{1}\cdot 5900$ and ϵ is equal to 0·39.

In this method it will be noticed (1) that the distribution of the ionisation is unimportant, (2) that the effect of diffusion is negligible, and (3) that there is no need of a constant source of radiation. This last condition was, however, fairly easily obtained with the special arrangement used for producing the break in the primary current of the induction coil.

3. *Experimental Arrangement.*

The diagram of the connections and the disposition of the apparatus is given in fig. 1. In the main it is the same as that used by Langevin, but certain

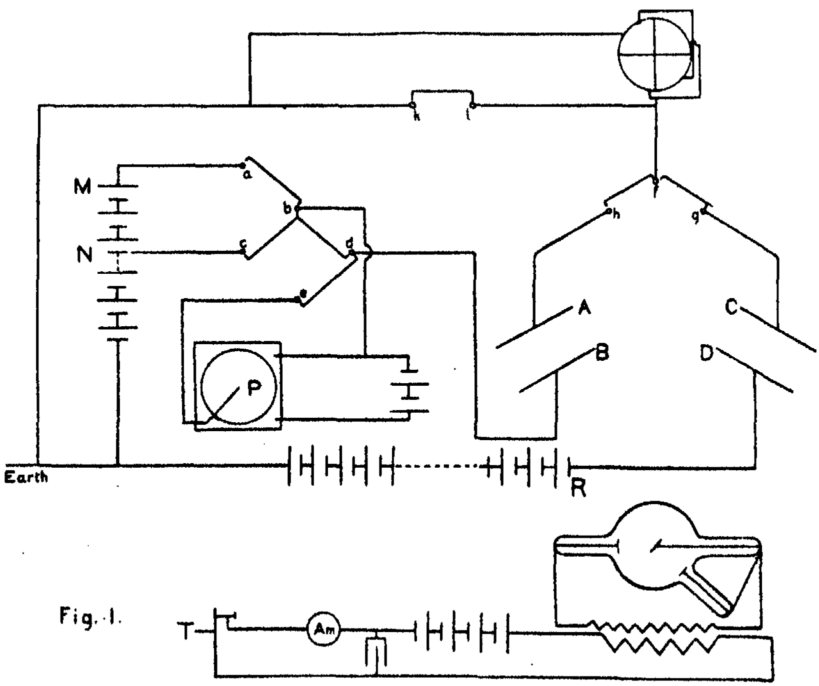


Fig. 1.

necessary modifications were introduced. A momentary discharge was produced in the Röntgen-ray bulb by the breaking of the contact at T, which was in the primary circuit of a Marconi induction coil. The contact at T was between two pieces of platinum which could be separated very suddenly. For effective action at this break it was necessary to have the platinum pieces held together by a steady, firm pressure. A capacity of about 8 microfarads was inserted in order to suppress the spark which would occur when the circuit

was broken. A small spark here gave great irregularities in the Röntgen-ray flash; however, when this was entirely eliminated, and with a constant current, as measured by the ammeter, in the primary, the ionisation produced in the chamber by a single flash of rays was very constant, and readings could be repeated with great ease.

The ionisation chambers are denoted by AB and CD. The upper electrodes A and C, by means of a key, could be connected, either separately or together, with the insulated pair of quadrants of the electrometer. Two exactly similar ionisation chambers were used and the Röntgen-ray bulb was adjusted so that the ionisation produced in each chamber by a single flash of the rays was the same. With electric fields of opposite sign in the two chambers, the electric charge received by the electrometer when connected with both chambers was zero. The quantity received in either of these chambers gives the charge Q_2.*

If the electric field in one chamber be now increased, one electrode receives a quantity of electricity Q_1 and the other a quantity Q_2 of opposite sign. If the two electrodes are both connected to the electrometer, the latter will suffer a deflection proportional to the difference of these charges, that is to Q_1-Q_2. This difference is a very small fraction of either of the charges Q_1 or Q_2 and the error in ϵ is approximately proportional to the error in Q_1-Q_2. It is better, therefore, to measure Q_1-Q_2 and Q_1 rather than Q_1 and Q_2 separately. Q_1-Q_2 may be only 1 or 2 per cent. of Q_1, and some special device is necessary if both quantities are to be measured with the same electrometer.

Langevin used an electrometer with a condenser of variable capacity. A similar method was first tried in these experiments but was not found to be very satisfactory. The variable capacity employed consisted of two sets of 10 parallel plates fixed to two axes. One set, which was connected with the electrometer, remained fixed; the other, which was kept at zero potential, could be rotated into or out of the fixed set, thus increasing or decreasing the capacity. In measuring the quantity Q_1, the condenser was

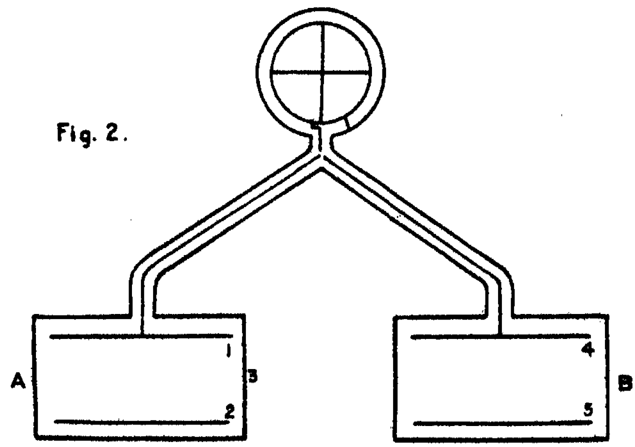
* The accumulation of the ions in the neighbourhood of the electrodes affects the electric field, which is no longer uniform but is of greater intensity in the vicinity of the electrodes. In the case of a uniform ionisation between the electrodes, Langevin has shown that the relative error resulting from the modification of the field by the ions has for its principal term and, at the same time, its upper limit, the value $Q_0/24\sigma$. The error, therefore, will be less than 1 per cent. so long as Q_0 does not exceed $\frac{1}{4}\sigma$. With a non-uniform ionisation the modification of the field by the ions becomes more important. At low pressures with small values of Q_1 and Q_2, Q_1-Q_2 becomes very small, and it is necessary to have larger values of the ratio Q/σ. In general, however, voltages were chosen so as to render the effect of the ionisation on the field practically negligible.

closed and the deflection of the electrometer observed when only one chamber was connected and a single flash used. At the same time a charge Q_2 of opposite sign had been communicated to the second chamber. This chamber was then connected to the electrometer, which gave a small deflection proportional to the charge $Q_1 - Q_2$. The movable set of plates of the condenser was revolved so as to decrease the capacity of the system. The deflection was now much greater and could be easily measured.

In using this method one serious difficulty was experienced which it was found impossible to eliminate entirely. This was an effect due to contact difference of potential. If the electrometer and large capacity system, initially connected to earth and then insulated, had its capacity decreased by opening the condenser, a deflection was always produced in the electrometer. Careful attention to the plates, etc., failed to eliminate this effect entirely. Apparently there was always a small difference of potential (probably some form of contact difference); and, on decreasing the capacity, this was revealed by the increased deflection. In certain cases this effect was an appreciable fraction of the deflection due to the charge $Q_1 - Q_2$. On this account another method was employed in which a variable condenser was done away with. All the charges to be measured were compensated by means of charges which were induced on the upper electrodes by varying the potential of the lower electrodes. The only quantities to be measured were potentials.

The method used was as follows:—

Fig. 2.



In fig. 2, A and B are the ionisation chambers. The plates 1 and 4 can be connected, either separately or together, to the electrometer, and the potential of the lower plate 2 can be varied. The outer case of the ionisation chambers,

the guard tubes T and T_1, one pair of quadrants, and the case of the electrometer, form part of one conductor kept at zero potential throughout the experiment. Suppose that, due to a single flash of Röntgen rays, the plate 1 receives a charge Q_1 and the plate 4 a charge Q_2. The quantities to be measured are the ratios $(Q_1-Q_2)/Q_1$ and Q_1/σ_1, where $4\pi\sigma_1 = X_1$, the electrostatic field between the plates 1 and 2 of the first chamber. Let $q_{11}, q_{21}, \ldots$, be the coefficients of capacity and induction of the systems of conductors, the suffixes referring to the numbers in the figure.

Let the plate 1 and the electrometer be insulated and the plate 4 be disconnected; the charge Q_0 on the conductor 1 is given by the relation

$$Q_0 = q_{11}V_1+q_{21}V_2+q_{31}V_3,$$

in which V_1, V_2 and V_3, are the potentials of 1, 2 and 3, respectively. Initially, V_1 and V_3 are both zero, so that the equation may be written

$$Q_0 = q_{21}V_2. \tag{4}$$

When the charge Q_1 is given to 1, let the potential of the electrometer become v. Then we have

$$Q_0+Q_1 = q_{11}v+q_{21}V_2. \tag{5}$$

Suppose now that the potential of 2 is changed to V_2+u, and that, in consequence, the potential of the electrometer becomes v_1, then, since there is no increase in the charge on 1, we have

$$Q_0+Q_1 = q_{11}v_1+q_{21}(V_2+u),$$

whence, subtracting (4),

$$Q_1 = q_{11}v_1+q_{21}u.$$

If u be adjusted so that the potential of the electrometer is brought back to zero, then

$$Q_1 = q_{21}u. \tag{6}$$

Similarly, when 1 and 4 are both connected to the electrometer

$$Q_0' = q_{11}V_1+q_{21}V_2+q_{54}V_4+q_{44}V_1,$$

and therefore

$$Q_0' = q_{21}V_2+q_{54}V_4, \quad \text{since } V_1 \text{ is zero.} \tag{7}$$

When the charge Q_1-Q_2 is given to 1, let the potential of the electrometer become v'. Then we have

$$Q_0'+(Q_1-Q_2) = q_{11}v'+q_{44}v'+q_{21}V_2+q_{54}V_4.$$

Suppose now, that the potential of 2 is changed to $V+u'$, and that the electrometer, in consequence, assumes a potential v_2'. We have

$$Q_0'+(Q_1-Q_2) = q_{11}v_2'+q_{44}v_2'+q_{21}(V_2+u')+q_{54}V_4, \tag{8}$$

and subtracting (7) from (8),

$$Q_1-Q_2 = q_{11}v_1'+q_{44}v_1'+q_{21}u'.$$

If u' be adjusted so that the potential of the electrometer is brought back to zero, this relation becomes

$$Q_1 - Q_2 = q_{21} u'. \tag{9}$$

Combining (6) with (9) we get the simple relation

$$\frac{Q_1 - Q_2}{Q_1} = \frac{u'}{u}. \tag{10}$$

Thus the ratio of the two charges is equal to the ratio of the potentials necessary to bring the potential of the electrometer back to zero in the two cases.

Again, in measuring the ratio Q_1/σ_1, connect 1, 2, 3, and 4 to earth, and then insulate 1 and 4, connection between the latter and the electrometer being broken. Now connect 2 to a potential U: there will be an induced charge on 1 and the electrometer will be deflected. The deflection in this will correspond to a charge σ_1 being given to the plate 1. The charge will also be given by $q_{21}U$, and combining this with (6) we have

$$\frac{Q_1}{\sigma_1} = \frac{u}{U}. \tag{11}$$

Thus the only quantities to be measured are the potentials U, u and u', and a sensitive electrometer of constant capacity can be used.

There are potentials of two orders of magnitude to be measured: one of the order of 1 volt and the other of the order of 100 volts. Voltages of both these orders, however, can easily be measured with an accuracy of 1 per cent. The low voltages were measured by comparison with a standard Weston cell. In practice the charges were not exactly neutralised, but the needle was brought very nearly back to the equilibrium position, and the small departures corrected for.

In order to reduce any small insulation leaks in the second chamber during the determination of the potential u, the charge Q_2 in this chamber could be nearly neutralised by changing the potential of the plate 4, and afterwards restored to its original value. By using this compensating method it was unnecessary to have the plates charged for any appreciable time, and therefore the effects of slight insulation leaks were reduced to a minimum. The manner in which the changes were brought about can be seen from the figure. The electrode B (fig. 1) was connected to the point d. When a and b and b and d were connected, B was at the potential of the plate M of the battery of cells. By breaking the contact between a and b, and joining c and b, the potential of B could be changed to that of the point N. P was a potentiometer consisting of 100 equal resistances. The current from a small number of accumulators passed through this, and, by moving

round the pointer, any fraction of this small potential could be added to or subtracted from that of the battery. By connecting *d* to *e* instead of *d* to *b*, the potential of the electrode could be changed by a small known amount. This was used in measuring the quantity $Q_1 - Q_2$. The potential of the electrode was determined by that of the battery. The small change of potential required to balance $Q_1 - Q_2$ was measured by means of a potentiometer and a Weston cell.

An experimental difficulty may be noticed here. If the gas between the plates was ionised while the plate A was insulated and the plate B was connected to earth, a deflection corresponding to a positive charge was produced in the electrometer. This effect was not due to a difference in the coefficients of diffusion of the positive and negative ions because an effect of a similar order of magnitude was obtained in carbon dioxide, in which gas the coefficients of diffusion of the two kinds of ions are very nearly the same. The effect was probably due to the emission of electrons from the upper electrode under the influence of the Röntgen rays. It was shown, however, that this effect did not influence the results obtained. The charge received by the upper electrode, when a single flash of Röntgen rays was used, was measured for gradually increasing electric fields, first in one direction and then in the opposite direction. For small values of the electric field the curves obtained were unsymmetrical, but this lack of symmetry decreased very rapidly as the potential increased, and for the large fields used in these experiments the two curves for electric fields of opposite sign were identical.

4. *Preparation of the Gases and Vapours.*

The atmospheric air was thoroughly dried before being admitted to the apparatus by allowing it to remain in contact with phosphorus pentoxide for some time. The carbon dioxide was liberated by the action of hydrochloric acid on calcium carbonate and was dried by allowing it to remain in contact with phosphorus pentoxide for some time. The carbon monoxide was liberated by the action of sulphuric acid on formic acid and was dried over phosphorus pentoxide. The sulphur dioxide was obtained from a cylinder of the liquid and was dried over phosphorus pentoxide. The nitrous oxide was obtained from a cylinder of the gas and was dried over phosphorus pentoxide. In some cases the gases were passed through a spiral tube immersed in liquid air. The ionisation chambers were exhausted by means of a Töpler pump, and the remaining gas was absorbed by means of charcoal immersed in liquid air. The dry gas was then admitted to the apparatus. In every case great care was taken to make the gas or vapour dust-free.

5. *Experimental Results.*

In order to test the law of recombination and the general theory of Langevin's method the experimental conditions were varied over as wide a range as possible. Such variations were obtained in the following ways:—

1. Different samples of the gas were experimented on and the experiments were repeated after long intervals.

2. With a given ionisation the electric fields were varied as widely as possible.

3. The intensity of the ionisation for a given sample of gas at a given pressure was varied.

4. Both chambers in turn were used as the standard, and the sign of the electric field was reversed.

5. Experiments were made at different pressures.

6. The distribution of the ionisation was varied. In some cases there was little secondary ionisation: this was the case when the upper electrode was aluminium, and also when it was arranged that the radiation did not fall on the electrode. When brass was used there was a large amount of secondary ionisation.

The results are given in Table I. The figures in the second column give the value of the coefficient ϵ at the pressures given in the first column. The third column gives the quotient of ϵ by the pressure, and the numbers in this column are proportional to the coefficient of recombination over the range for which the mobility is inversely proportional to the pressure. In the fourth column is given the value of the quotient of ϵ by the square of the pressure.

Each result represents the mean of a large number of observations made under widely different conditions, and, in many cases, after long intervals of time. Under conditions so varied as those enumerated above it was only to be expected that some variations would occur: the greater number of these variations, however, were within 5 or 6 per cent. of the mean value.

The values apply to a mean temperature of about 15° C. The temperature at the time of the observations was always recorded, but no correction was made as it was considered that such a correction would almost certainly be within the limits of error of the experiment.

6. *Discussion of Results.*

From this table it will be seen that the coefficient ϵ is very nearly proportional to the square of the pressure over a fairly wide range of pressures. At higher pressures this rate of increase becomes smaller.

Table I.

Pressure in mm.	ϵ.	ϵ/p.	ϵ/p^2.
	Air.		
743	0·272	368	495
662	0·215	325	491
644	0·204	318	494
462	0·104	226	488
363	0·067	182	508
307	0·050	161	530
197	0·019	96	490
	Carbon Dioxide.		
729	0·529	725	996
614	0·390	635	1035
498	0·261	525	1054
373	0·151	406	1085
265	0·078	294	1110
175	0·038	217	1240
	Carbon Monoxide.		
757	0·215	284	375
690	0·172	250	362
556	0·114	205	369
409	0·059	145	354
247	0·018	73	295
	Sulphur Dioxide.		
680	0·765	1125	165
504	0·466	924	184
444	0·346	780	175
338	0·21	620	182
200	0·072	360	180
83·5	0·019	225	269
	Nitrous Oxide.		
749	0·431	575	770
596	0·291	488	821
430	0·148	344	802
294	0·073	245	845
200	0·028	140	700

Such a departure is to be expected if we accept Langevin's interpretation of ϵ, for it would tend to approach a limit when every collision is accompanied by recombination. Under these circumstances ϵ would be unity, and a further increase in the pressure would produce no increase in the value of ϵ. This limit appears to be reached for comparatively small pressures:—in air at a pressure of about 4 or 5 atmospheres; in sulphur dioxide at an even lower pressure.

The Absolute Values of the Coefficient of Recombination.—The absolute values of the coefficient of recombination were calculated from the relation

$$\alpha = 4\pi(k_1+k_2)\,ee,$$

in which k_1 and k_2 are the mobilities of the positive and negative ions, and e is the electronic charge measured in electrostatic units. The mobilities have been determined with great accuracy for a large number of gases and vapours by Wellisch,* and the values determined by him were used. The values of α in terms of e are given in Table II. The results of Langevin and others on air and carbon dioxide at atmospheric pressure are also included in this table. The results are shown graphically in fig. 3.

Table II.

Air.

Pressure	743	662	644	462	363	307	197
Coefficient of recombination	3500	3090	3020	2150	1730	1530	920

Carbon Dioxide.

Pressure	729	614	498	373	265	175
Coefficient of recombination	3440	3020	2500	1930	1400	1020

Carbon Monoxide.

Pressure	757	690	556	409	247
Coefficient of recombination	1820	1600	1310	930	468

Sulphur Dioxide.

Pressure	680	504	444	338	200	83·5
Coefficient of recombination	2740	2250	1900	1510	876	548

Nitrous Oxide.

Pressure	749	596	430	204	200
Coefficient of recombination	2830	2400	1690	1110	690

	Air.	Carbon dioxide.
Townsend	3420	3500
McClung	3384	3492
Langevin	3200	3400

There is a good agreement between the results obtained by different observers working with air and carbon dioxide at atmospheric pressure. This is more striking when one considers the great difference between the method employed in the experiments described in this paper for example, and that employed by McClung.

At low pressures, however, there are wide divergences. From the curves

* 'Phil. Trans.,' A, vol. 209.

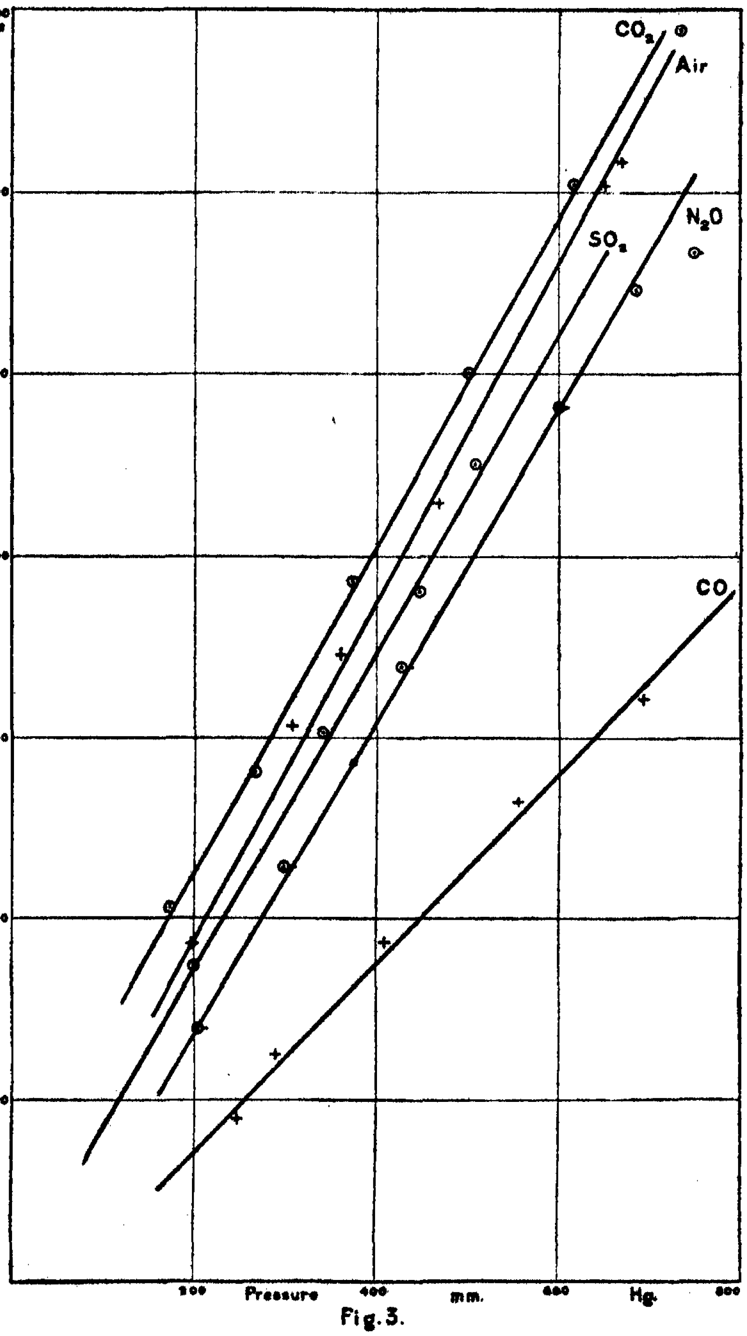


Fig. 3.

it can be seen that, for a considerable range of pressure, depending on the gas, the coefficient of recombination is proportional to the pressure. This

range seems to be less in the case of those gases for which ϵ is large. At higher pressures, we have seen that ϵ approaches a maximum value equal to unity. The mobility of the ion, however, as Kovarik* has shown, varies inversely as the pressure over a range of pressures of 50 atmospheres. Thus the curve connecting the coefficient of recombination with the pressure will, at first, be a straight line, and afterwards will pass through a maximum value. At high pressures a very small value for the coefficient would be expected.

Many years ago Bragg showed that, in the case of the recombination of the ions produced by α-rays, there existed certain peculiarities in the initial stages of the recombination. Plimpton has very recently shown that similar peculiarities occur when the ionising agent is Röntgen rays. The abnormally high results obtained by these authors are very probably due to the fact that, in the initial stages, the ions are confined along the tracks of the electrons ejected from the molecules and, in general, the distance between an initial pair of ions would be less than the distance between the ions at a later stage.

In the method employed in the experiments described in this paper, this effect does not come in to any appreciable extent. In the first place, a uniform distribution of ions is unnecessary, and in the second place, the peculiar distribution of the ions characteristic of the ionisation by the moving particles ejected by the Röntgen rays would disappear almost instantaneously in the presence of the large electric fields used. This is supported by the agreement between the results of the experiments made under different experimental conditions; large variations of the electric field and of the intensity of the ionisation do not seem to produce any appreciable effect on the coefficient of recombination. Although for this reason the results obtained by Plimpton cannot be compared with those described here, one point may be noticed. As would be expected, Plimpton's values are in every case very large, but these values decrease when the time-interval during which diffusion is allowed to take place is increased. The final slopes of the curves obtained from Plimpton's data, however, are too steep to enable one to deduce a limiting value with any degree of accuracy. This is especially so in the case of carbon dioxide, in which the coefficient of diffusion is much smaller than it is in air. The final value obtained is 4880 compared with an initial value of 10,000, and the value is still decreasing. In the case of air the lowest value for α is 3960. This value is about 10 per cent. higher than the result given here.

The values of ϵ obtained at low pressures in these experiments may be

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 154.

briefly mentioned here. The observations at low pressures are much more difficult than those at higher pressures, especially in those gases in which the ionisation is small. The important quantity which has to be measured is $Q_1 - Q_2$, the difference between the quantities of electricity which reach the electrode for two different values of the field. This quantity depends on the value of the coefficient ϵ and on the ionisation in the gas. Both these decrease when the pressure decreases, the former being approximately inversely proportional to the square of the pressure. At low pressures, therefore, the difference $Q_1 - Q_2$ becomes very small. This difficulty can be obviated to some extent by using more than one flash of the rays, but this is not so satisfactory.

The results obtained do seem to indicate departures from the linear law at lower pressures, but in view of the increased difficulty of the experiments it is perhaps well not to lay too much emphasis on these variations. It is significant, however, that the changes appear in the region of pressure in which other experiments seem to suggest that some modification takes place in the negative ion.

The constancy of the results that have been obtained in these experiments under conditions which have been very widely varied seems to be in favour of the simple law of recombination

$$\frac{dn}{dt} = -\alpha n^2,$$

or in its more general form,

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}.$$

Among the modifications of this law which have been proposed, perhaps the best known is that of Sutherland

$$\frac{dn}{dt} = -\alpha n^{5/3}.$$

It is not always easy to distinguish between these two laws, and the results of some observers seem to fit in almost equally well with both formulæ. Experiments in which ionisation of very widely varying intensity is used seem most promising. It is hoped to give a more detailed account of some experiments on this point at a later date.

7. *Conclusions.*

(1) Recombination appears to take place according to the simple law

$$\frac{dn}{dt} = -\alpha n^2,$$

or more generally

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = -\frac{dn_2}{dt}.$$

(2) The coefficient of recombination varies with the pressure and throughout a considerable range of pressure is proportional to the pressure.

In conclusion I desire to express my appreciation of the kindly interest which Prof. Sir J. J. Thomson has shown throughout this work.

The Flexure of Telescope Mirror-discs Arising from their Weight, and its Influence upon Resolving Power.

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The resolving power of a reflecting telescope is proportional to its aperture, the mirror being supposed accurately a paraboloid of revolution, so that a bundle of parallel rays pass through a geometrical focus after reflection. Regarded from this point of view alone it is of advantage, in the construction of a reflecting telescope, to make the mirror of as large a size as the mechanical difficulties incident to the construction of large mirrors will allow, difficulties, that is to say, such as that of obtaining the glass of the necessary homogeneity throughout, in order to avoid distortion owing to changes of temperature, and the difficulties of grinding, shaping, and polishing. There is, however, another factor to be considered which affects the problem. The mirror, even if perfect in other respects, will, when partially supported, be distorted by its weight, to a greater or less extent according to the nature of the support. This distortion will cause a diminution in the resolving power, the effect of which will evidently increase with the size of the mirror, and so will tend to counteract the advantage accruing from the larger aperture. It is conceivable even that there will, for any

given method of support, be a critical aperture, an increase of the size of the mirror beyond which will actually produce a decrease instead of an increase in the resolving power. The object of the present paper is, firstly, to calculate the nature and amount of the distortion which is produced by the weight for various methods of support, and, secondly, to investigate to what extent this distortion will affect the resolving power of the instrument, and whether any limitation is thereby placed upon the size of the mirrors which are likely to be practically attainable. The types of support which are considered are necessarily comparatively simple and somewhat ideal: the difficulties of the mathematical analysis impose these limitations, but it will be seen that they are sufficient to enable us to give a definite answer to the problem as to whether the critical size of aperture is one which is likely to be reached in the construction of large mirrors, or as to whether this critical size is so large as to be of no practical significance.

Since the equations of elastic equilibrium are linear it is sufficient to consider the flexure of the disc for the two cases in which it is horizontal and vertical. The case in which it is inclined at any angle can then be obtained by a combination of these. The notation used throughout will be that used by Prof. Love in his 'Mathematical Theory of Elasticity.'*

We will discuss first the case in which the plane of the disc is horizontal, and will treat it as a circular plate of uniform thickness. This is nearly true for large mirrors and will be a sufficient approximation for the present discussion. We consider several different supports.

(1) The disc is held in a horizontal position, being supported at its centre, its edge being free.

We obtain the solution by a combination of various stress systems, which together are to give the correct body forces and are to be so adjusted as to satisfy the terminal conditions.

The conditions in this case are that the normal displacement at the centre should vanish, and that the stress resultants, and stress couples, T, S, G,† should vanish at the edge.

We use the following systems of stress—

(α) A system in which all the stress components vanish except

$$Z_z = w(z+h),$$

w being the weight of the plate per unit volume, and the z axis being vertically upwards, and the origin in the central plane. $2h$ is the thickness of the plate.

* Camb. Univ. Press, 1906, 2nd Edition.

† *Vide* Love, *loc. cit.*, § 294.

The corresponding displacements may be taken to be given by

$$u = -\frac{\sigma w}{E}(z+h)x, \qquad v = -\frac{\sigma w}{E}(z+h)y,$$

$$w = \frac{w}{2E}\{z^2+2hz+\sigma(x^2+y^2)\}.$$

Also all stress resultants are zero.

The axes of x and y are in the plane of the plate; u, v, w are the components of displacement parallel to the three axes; σ, E, as usual, denote Poisson's Ratio and Young's Modulus of Elasticity for the material of the plate.

(β) A stress-system in which there is a pressure $2wh$ on the face $z = h$ of the plate. The solution for a plate bent by a uniform pressure over one face is given in Love, § 307; we must in the solution there given put $p = 2wh$ and so obtain

$$u = -\frac{1+\sigma}{E}\cdot\frac{wx}{4h^2}[(2-\sigma)z^3-3h^2z-2h^3-\tfrac{3}{4}(1-\sigma)z(x^2+y^2)],$$

$$v = -\frac{1+\sigma}{E}\cdot\frac{wy}{4h^2}[(2-\sigma)z^3-3h^2z-2h^3-\tfrac{3}{4}(1-\sigma)z(x^2+y^2)],$$

$$w = \frac{1+\sigma}{E}\cdot\frac{w}{8h^2}[(1+\sigma)z^4-6h^2z^2-8h^3z+3(h^2-\sigma z^2)(x^2+y^2) \\ -\tfrac{3}{8}(1-\sigma)(x^2+y^2)^2].$$

$$T_1 = wh^2 = T_2, \quad S_1 = 0, \quad N_1 = whx, \quad N_2 = why.$$

$$G_1 = \frac{wh}{8}\{(3+\sigma)x^2+(1+3\sigma)y^2\}+\frac{3-\sigma}{10}wh^3.$$

$$G_2 = \frac{wh}{8}\{(1+3\sigma)x^2+(3+\sigma)y^2\}+\frac{3-\sigma}{10}wh^3.$$

$$H_1 = -\frac{1-\sigma}{4}whxy.$$

These give, in the central plane $z = 0$, a radial displacement of amount $\frac{1+\sigma}{2E}whr$, and a normal displacement

$$\mathsf{W} = -\frac{wh}{32D}(x^2+y^2)\left(x^2+y^2-\frac{8h^2}{1-\sigma}\right),$$

where $D = \frac{2}{3}Eh^3/(1-\sigma^2)$ is the flexural rigidity of the plate.

If the radius of the plate be b, we have also at the edge

$$G = \frac{3+\sigma}{8}whb^2+\frac{3-\sigma}{10}wh^3,$$

$$T = wh^2, \quad S = 0, \quad N = whb.$$

(γ) We need other solutions which give no resultant body forces in order to adjust the boundary conditions.

We may take

$$u = -\frac{1-\sigma}{2E}whx, \quad v = -\frac{1-\sigma}{2E}why, \quad w = -\frac{\sigma}{E}whz,$$

giving $$G = 0, \quad N = 0, \quad T = wh^2.$$

For this system the normal displacement of the central plane vanishes, but there is a radial displacement in the plane of amount $-\frac{1-\sigma}{2E}whr$.

(δ) We finally take the solution corresponding to a system of generalised plane stress, given in Love, §§ 303 and 304.

The components of displacement in the central plane vanish. If $\mathbf{W}$ is the normal displacement of the central plane it is shown that $\mathbf{W}$ satisfies

$$\nabla^2\nabla^2\mathbf{W} = 0,$$

where ∇^2 is Laplace's Operator in two dimensions, and that the stress resultants are derived, when $\mathbf{W}$ is known, from the formulæ

$$T = S = 0, \quad N = -D\frac{d}{dr}(\nabla^2\mathbf{W}).$$

$$G = -D\nabla^2\mathbf{W} + \frac{D}{r}(1-\sigma)\frac{d}{dr}\left(\mathbf{W} + \frac{8+\sigma}{10(1-\sigma)}h^2\nabla^2\mathbf{W}\right).$$

We have $\mathbf{W}$ given by an expression of the form

$$\mathbf{W} = \frac{A}{2}\left\{\frac{r^2}{2}(\log r - \tfrac{1}{2}) - \frac{r^2}{4}\right\} + \frac{Br^2}{4},$$

since $\mathbf{W}$ vanishes at the centre. Therefore

$$G = -D\{A\log r + B\} + \frac{D(1-\sigma)}{r}\left\{\frac{Ar}{2}(\log r - \tfrac{1}{2}) + \frac{Br}{2} + \frac{1}{10}\cdot\frac{8+\sigma}{1-\sigma}h^2\frac{A}{r}\right\}.$$

Combining these four solutions, the conditions that G, N vanish at the edge give

$$A = whb^2/D, \quad B = whb^2\left\{-(1+\sigma)\log b + \tfrac{1}{4}(1+3\sigma) + \frac{11h^2}{5b^2}\right\}\Big/ D(1+\sigma).$$

The total value of $\mathbf{W}$ at any point is

$$-\frac{wh}{32D}r^2\left(r^2 - \frac{8h^2}{1-\sigma}\right) + \frac{w\sigma}{2E}r^2 + \frac{Ar^2}{4}(\log r - 1) + \frac{Br^2}{4},$$

i.e. there is a downward displacement at any point of amount

$$\mathbf{W} = \frac{3w(1-\sigma)}{64Eh^2}r^2\{(1+\sigma)r^2 + 2(3+\sigma)b^2\} - \frac{3w(1-\sigma^2)b^2r^2}{8Eh^2}\log\frac{r}{b} - \frac{24+\sigma}{20E}wr^2.$$

Putting $2whb^2 = W$, the weight of the plate, the downward deflection at the edge is given by

$$\mathbf{W}_{edge} = \frac{3Wb^2}{128\pi Eh^3}(1-\sigma)(7+3\sigma) - \frac{W}{40\pi Eh}(24+\sigma).$$

The second term in this expression is small compared with the first, the relative magnitudes being of the order h^2/b^2, which is comparatively small, since the usual order of magnitude of the thickness is 1/10 of the aperture.

The correctness of the first term of this expression can be proved by the use of the approximate theory which holds for the flexure of plates. This approximate theory is very useful in obtaining solutions for more complicated cases of support, when the more exact theory would either be very tedious or else impracticable.

It is shown by Love* that for a plate slightly bent by transverse forces only the stress couples at the edge are given by

$$G = -D\left\{\frac{\partial^2 \mathbf{W}}{\partial \nu^2} + \sigma\left(\frac{\partial^2 \mathbf{W}}{\partial s^2} + \frac{1}{\rho}\cdot\frac{\partial \mathbf{W}}{\partial \nu}\right)\right\},$$

$$H = D(1-\sigma)\frac{\partial}{\partial \nu}\left(\frac{\partial \mathbf{W}}{\partial s}\right), \qquad N = -D\frac{\partial}{\partial \nu}(\nabla^2 \mathbf{W}),$$

where $\partial/\partial\nu$ denotes differentiation along the outward normal at the edge, and $\partial/\partial s$ along the edge, ρ is the radius of curvature.

If Z is the acting force per unit area, $\mathbf{W}$ is determined by

$$D\nabla^4 \mathbf{W} = Z.$$

We therefore have for the case of a circular plate under the action of its own weight,

$$\frac{1}{r}\cdot\frac{d}{dr}\left[r\frac{d}{dr}\left\{\frac{1}{r}\cdot\frac{d}{dr}\left(r\frac{d\mathbf{W}}{dr}\right)\right\}\right] = \frac{W}{\pi b^2 D};$$

so that
$$\mathbf{W} = \frac{Wr^4}{64\pi b^2 D} + \frac{A}{2}\left\{\frac{r^2}{2}(\log r - \tfrac{1}{2}) - \frac{r^2}{4}\right\} + \frac{Br^2}{4},$$

using the fact, where necessary, in the integration that $\mathbf{W}$ vanishes at the centre of the plate: so that when $r = b$ we must have, since G, N vanish at the boundary,

$$A = -\frac{W}{2\pi D} \quad \text{and} \quad B = -\frac{W}{2\pi D(1+\sigma)}\left\{-(1+\sigma)\log b + \frac{1+3\sigma}{4}\right\}.$$

These values of A, B agree in magnitude with those previously obtained, provided that the term in B which involves h^2 be neglected.

We therefore obtain the deflection at the edge given by the approximate expression

$$\mathbf{W} = \frac{Wb^2}{64\pi D}\cdot\frac{7+3\sigma}{1+\sigma}.$$

* *Loc. cit.*, § 313.

(2) We now take the case in which the plate is held horizontally and clamped at the rim.

Then we must have both $\mathbf{W}$ and $d\mathbf{W}/dr$ vanishing at points on the rim; and the radial displacement in the plane of the disc must also vanish on the rim.

If we combine the system of solutions (α)–(δ) above, the resultant radial displacement is

$$\frac{wh}{2E} r\{-2\sigma+1+\sigma-(1-\sigma)\},$$

and so vanishes at all points.

We may take for the solution of $\nabla^2\nabla^2\mathbf{W} = 0$ in (δ) in this case

$$\mathbf{W} = \frac{A}{2}\left[\frac{r^2}{2}(\log r - \tfrac{1}{2}) - \frac{r^2}{4}\right] + \frac{Br^2}{4} + C\log r + F.$$

Since $\mathbf{W}$ is not infinite at the centre, we must have $C = 0$, and in order that G may not become infinite at the centre, we must have $A = 0$.

Thus the conditions $\mathbf{W} = 0$, $d\mathbf{W}/dr = 0$ at $r = b$ require that

$$B = -\frac{2w\sigma}{E} + \frac{wh}{4D}\left(b^2 - \frac{4h^2}{1-\sigma}\right), \qquad F = -\frac{whb^4}{32D},$$

and the depression at any point is given by

$$\mathbf{W} = \frac{W}{64\pi b^2 D}(b^2-r^2),$$

the central depression being $Wb^2/64\pi D$.

In this case the exact theory agrees with the approximate theory.* The reason is that no terms depending upon h^2 are involved.

(3) If the plate is supported at the edge, we must have T, S, G, $\mathbf{W}$ vanishing there. The first two evidently do so.

We can take the same solution for $\mathbf{W}$ as in (2), and the remaining conditions give

$$B = \frac{3+\sigma}{4(1+\sigma)D} whb^2 + \frac{3-\sigma}{5(1+\sigma)D} wh^3$$

and

$$-F = \frac{wb^4h}{32D}\cdot\frac{5+\sigma}{1+\sigma} + \frac{wb^2h^3}{480D(1-\sigma^2)}(87+79\sigma+24\sigma^2),$$

giving for the value of $\mathbf{W}$ at any point, a downward displacement,

$$\mathbf{W} = \frac{wh}{32D}\{b^2-r^2\}\left\{\frac{5+\sigma}{1+\sigma}b^2 - r^2\right\} - \frac{wh^3}{60(1-\sigma^2)}\left\{(3\sigma^2+23\sigma+24)r^2 - \frac{(87+79\sigma+24\sigma^2)b^2}{8}\right\}.$$

* See solution, in Love, p. 467 (ii).

The first term agrees with that obtained by means of the approximate theory.

Combining these three results we have, for the relative depressions of centre and rim,

(1) When supported at the centre,

$$\frac{3Wb^2}{128\pi Eh^3}(1-\sigma)(7+3\sigma)-\frac{W}{40\pi Eh}(24+\sigma).$$

(2) When clamped at the rim,

$$\frac{3Wb^2}{128\pi Eh^3}(1-\sigma^2).$$

(3) When supported at the rim,

$$\frac{3Wb^2}{128\pi Eh^3}(1-\sigma)(5+\sigma)+\frac{W}{640\pi Eh}(87+79\sigma+24\sigma^2).$$

Neglecting the small second term, the ratios of these expressions depend only upon the value of σ. If we put $\sigma=\frac{1}{4}$, which is approximately the case for glass, we have the relative deflections in these three cases given by the ratios

$$93:15:63.$$

The deflection is thus much smaller in the case of the clamped rim.

(4) It is to be expected that the more complete the support at the back of the mirror the less will be the effect due to the flexure. We will accordingly consider the case in which the plate is not only supported at the centre, so that there $\mathbf{W}=0$, but is, in addition, supported at the edge.

A sufficiently close value of the flexure is obtained by using the approximate theory, and since the work is much shortened by so doing, that is the course here adopted. We have

$$\nabla^4\mathbf{W}=\frac{W}{\pi b^2 D}.$$

Thus $$\mathbf{W}=\frac{Wr^4}{64\pi b^2 D}+\frac{A}{4}r^2(\log r-1)+\frac{Br^2}{4}+C\log r+D.$$

Since $\mathbf{W}=0$ at the centre, we must put $C=D=0$; and since $\mathbf{W}=0$ at the edge $r=b$, we obtain

$$\frac{W}{16\pi D}+A(\log b-1)+B=0.$$

Also $G=-D\left(\frac{d^2\mathbf{W}}{dr^2}+\frac{\sigma}{r}\cdot\frac{d\mathbf{W}}{dr}\right)$ must vanish at the edge.

The second boundary condition is accordingly

$$\frac{\sigma+3}{8\pi D}W+A\left\{(\sigma+1)\log b+\frac{1-\sigma}{2}\right\}+B(1+\sigma)=0.$$

From these two equations we obtain

$$A = -\frac{5+\sigma}{3+\sigma} \cdot \frac{W}{8\pi D},$$

$$B = -\frac{13+3\sigma-2(5+\sigma)\log b}{3+\sigma} \cdot \frac{W}{16\pi D},$$

and the value of $\mathbf{W}$ at any point of the plate is given by

$$\mathbf{W} = \frac{3(1-\sigma^2)W}{128\pi Eh^3b^2}r^2(r^2-b^2) - \frac{3W(1-\sigma^2)(5+\sigma)}{64\pi Eh^3(3+\sigma)}r^2\log\frac{r}{b},$$

which vanishes—as it should—when $r = 0, b$.

(5) We consider finally, as an example of a still more complete support, the case in which the disc of radius b is supported at the centre and the edge, and also round the circumference of a concentric circle of radius c.

We must now assume different solutions which hold according as $r \gtrless c$.

If $r < c$ we may assume

$$\mathbf{W}_1 = \frac{Wr^4}{64\pi b^2 D} + Ar^2(\log r - 1) + Br^2,$$

$$G_1 = -D\left\{\frac{3Wr^2}{16\pi b^2 D} + 2A(\log r + \tfrac{1}{2}) + 2B + \sigma\left(\frac{Wr^2}{16\pi b^2 D} + 2A(\log r - \tfrac{1}{2}) + 2B\right)\right\}$$

$$= -D\left\{\frac{(\sigma+3)Wr^2}{16\pi b^2 D} + 2A\left((1+\sigma)\log r + \frac{1-\sigma}{2}\right) + 2B(1+\sigma)\right\}.$$

If $r > c$ we take

$$\mathbf{W}_2 = \frac{Wr^4}{64\pi b^2 D} + A'r^2(\log r - 1) + B'r^2 + C'\log r + D',$$

$$G_2 = -D\left\{\frac{(\sigma+3)Wr^2}{16\pi b^2 D} + 2A'\left((1+\sigma)\log r + \frac{1-\sigma}{2}\right) + 2B'(1+\sigma) - \frac{C'}{r^2}(1-\sigma)\right\}$$

We have here six constants occurring. These are uniquely determined from the six boundary conditions, which are that

(α) $\mathbf{W}_1$, $\mathbf{W}_2$, should vanish when $r = c$,

(β) $\dfrac{d\mathbf{W}_1}{dr} = \dfrac{d\mathbf{W}_2}{dr}$ when $r = c$, (γ) $\mathbf{W}_2 = 0$ when $r = b$.

(δ) $G_1 = G_2$ „ $r = c$, (ϵ) $G_2 = 0$ „ $r = b$.

The condition that $\mathbf{W}_1 = 0$ when $r = 0$ has been satisfied already by our choice of $\mathbf{W}_1$.

From these equations we deduce that

$$A = A' - \frac{C'}{c^2}, \qquad B = B' + \frac{C'}{c^2}\log c,$$

$$D' = -C'(\log c - 1),$$

and also that

$$A' \Big/ \left[\{(2\sigma+10)b^2-(\sigma+3)c^2\}(b^2-c^2)-\{\tfrac{1}{2}(\sigma+3)b^2-(2+2\sigma)c^2\}c^2\log\frac{b}{c} \right]$$

$$= C' \Big/ \left[b^2c^2\left\{(2\sigma+10)b^2\log\frac{b}{c}-(3+\sigma)(b^2-c^2)\right\}\right]$$

$$= \frac{W}{64\pi b^2 D} \Big/ \left[\left\{2(\sigma+3)\log\frac{b}{c}+2(1+\sigma)\log^2\frac{b}{c}\right\}c^2-(3+\sigma)(b^2-c^2)\right].$$

These equations suffice to determine the deflection at any point of the disc in this case.

We have still to consider the solutions of the stress equations which are appropriate to the case in which the disc is held vertically. The body forces are now in the plane of the disc, and there are no normal components. We take the x and y axes in the plane, the origin being at the centre, and the positive direction of the x axis being vertically downwards. We will consider several simple solutions, by a combination of which the solutions appropriate to various boundary conditions may be obtained.

We take the following simple solutions of the state of plane stress:—

(α) If we assume

$$X_x = -\frac{wx}{2}, \qquad Y_y = \frac{wx}{2}, \qquad X_y = -\frac{wy}{2},$$

we have a system of stresses which give a body force parallel to the x axis of amount $+w$, the weight per unit area. The remaining solutions will, therefore, be such as to give no resultant body forces.

From these values we deduce the following particular solutions for the displacements,

$$u = -\frac{w}{4E}(1+\sigma)(x^2+y^2), \qquad v = \frac{w(1+\sigma)}{2E}xy, \qquad w = 0,$$

and the stress resultants are

$$T_1 = -whx, \qquad T_2 = whx, \qquad S_1 = -S_2 = -why,$$

which give $\qquad T = -whr\cos\theta, \qquad S = whr\sin\theta,$

and G, H, etc., all zero.

(β) A particular solution which gives no body forces is one in which the stress resultants and the components of displacement are given by

$$u = \frac{w}{4E}(\sigma z^2-\sigma x^2-y^2), \qquad v = \frac{w}{2E}xy, \qquad w = -\frac{\sigma w}{2E}xz,$$

and $\qquad T_1 = 0, \qquad T_2 = whx, \qquad S_1 = 0,$

and the rest zero. Thus

$$T = whx\sin^2\theta = whr\sin^2\theta\cos\theta.$$
$$S = \tfrac{1}{2}whx\sin 2\theta = whr\sin\theta\cos^2\theta.$$

(γ) There are also a series of particular solutions for forces in the plane of the disc which are given by

$$T_1 = -T_2 = 2h\frac{\partial^2\chi}{\partial y^2}, \qquad S_1 = -2h\frac{\partial^2\chi}{\partial x\partial y},$$
$$u = -\frac{1+\sigma}{E}\cdot\frac{\partial\chi}{\partial x}, \qquad v = -\frac{1+\sigma}{E}\cdot\frac{\partial\chi}{\partial y},$$

where χ is any plane harmonic function.

These values give

$$T = 2h\left\{\cos 2\theta\frac{\partial^2\chi}{\partial y^2} - \sin 2\theta\frac{\partial^2\chi}{\partial x\partial y}\right\},$$
$$S = -2h\left\{\sin 2\theta\frac{\partial^2\chi}{\partial y^2} + \cos 2\theta\frac{\partial^2\chi}{\partial x\partial y}\right\}.$$

If we take $\chi = w(\tfrac{1}{6}x^3 - \tfrac{1}{2}xy^2)$, a plane harmonic of the third degree, we obtain

$$T = 2hw\{-\cos 2\theta . x + \sin 2\theta . y\} = -2whr\cos 3\theta,$$
$$S = 2hw\{\sin 2\theta . x + \cos 2\theta . y\} \quad = 2whr\sin 3\theta.$$

and then the displacements are

$$u = -\frac{1+\sigma}{2E}w(x^2-y^2) = -\frac{1+\sigma}{2E}wr^2\cos 2\theta,$$
$$v = \frac{1+\sigma}{E}wxy \qquad = \frac{1+\sigma}{2E}wr^2\sin 2\theta.$$

(δ) If the plate is held at the centre there must be a force applied there which is equal in magnitude to the weight of the disc. The simplest case of a singularity arising from the application of a force at a point inside the body is given in Love, § 148.

The components of displacement are

$$u = \frac{(3-\sigma)(1+\sigma)}{2E}A\log r + \frac{(1+\sigma)^2}{2E}\cdot A\frac{y^2}{r^2}, \qquad v = -\frac{(1+\sigma)^2}{2E}\cdot A\frac{xy}{r^2},$$

and the stress components are given by

$$X_x = A\frac{x}{r^2}\left(\frac{\sigma+3}{2} - (1+\sigma)\frac{y^2}{r^2}\right),$$
$$Y_y = A\frac{x}{r^2}\left(-\frac{1-\sigma}{2} + (1+\sigma)\frac{y^2}{r^2}\right),$$
$$X_y = A\frac{y}{r^2}\left(\frac{1-\sigma}{2} + (1+\sigma)\frac{x^2}{r^2}\right).$$

These are easily shown to give

$$T = 2hA\frac{\sigma+3}{2}\cdot\frac{\cos\theta}{r}, \qquad S = -2hA\frac{1-\sigma}{2}\cdot\frac{\sin\theta}{r}.$$

(1) We combine these solutions by adding to the first, the second multiplied by a constant l, m times the third, and n times the fourth. Then the stress components are found to vanish all round the edge provided that $l = -2(1+\sigma)$, $m = (1+\sigma)/4$, $n = wb^2/2\mathrm{A}$.

The coefficient in the stress resultants in the solution (δ) is then $wb^2/2\mathrm{A}\,.\,2h\mathrm{A} = whb^2$. The resultant of the tractions on the surface of a small cavity taken round the point of application of the applied force must be equal and opposite to that force, and therefore independent of the shape of the cavity in the limit when its dimensions are taken very small.

The resultant is easily found to be $-\pi wa^2\,.\,2h$ parallel to the positive direction of the x axis, and is therefore equal in magnitude and opposite in direction to the weight of the body, and so is correct.

The solution thus obtained is therefore the correct solution for the case in which the disc is supported at its centre with its edge free. The displacement components are given by

$$u = \frac{w(1+\sigma)}{8\,\mathrm{E}}\{-3(1-\sigma)x^2+(3+\sigma)y^2-4\sigma z^2\}+\frac{wb^2}{4\mathrm{E}}(1+\sigma)^2\frac{y^2}{r^2}$$
$$+\frac{wb^2}{4\,\mathrm{E}}(3-\sigma)(1+\sigma)\log r+\text{const.}$$

$$v = -\frac{1-\sigma^2}{4\,\mathrm{E}}wxy-\frac{(1+\sigma)^2}{4\mathrm{E}}w\frac{b^2}{r^2}xy.$$

The constant occurring in the expression for u has to be determined from the condition that u should vanish when r vanishes; but on account of the logarithmic term u becomes infinite at the centre. The reason for this is that the force cannot be applied at an exact mathematical point: it must be distributed over a small area, and the value of the constant will depend upon the mode of this distribution. The difference of the displacements in the direction of the force at any two points on the disc can, however, be uniquely determined by this formula.

(2) If the disc is clamped at the edge and held vertically the displacements there must be zero. To obtain the appropriate solution we combine the cases (α), (β), (γ) above, determining the constants introduced by means of the boundary conditions; we obtain

$$u = -\frac{w}{4\mathrm{E}}(1+\sigma)(x^2+y^2)+l\frac{w}{4\mathrm{E}}(\sigma z^2-\sigma x^2-y^2)-m\frac{(1+\sigma)}{2\mathrm{E}}w(x^2-y^2)+\text{const.}$$

$$v = \frac{w(1+\sigma)}{2\,\mathrm{E}}xy+l\frac{w}{2\mathrm{E}}xy+m\frac{1+\sigma}{\mathrm{E}}wxy.$$

$$w = -l\frac{\sigma w}{2\mathrm{E}}xr.$$

We choose l, m so that the coefficients of x^2, y^2 in the expression for u are equal, and so that v vanishes, *i.e.*

$$l = -\frac{2(1+\sigma)}{3-\sigma}, \qquad m = -\frac{1-\sigma}{2(3-\sigma)}.$$

The constant in u is so chosen that u is zero on the rim.

We thus obtain

$$u = \frac{(1-\sigma^2)\,w}{2\mathrm{E}\,(3-\sigma)}(b^2-x^2-y^2) - \frac{(1+\sigma)\,\sigma w}{2\mathrm{E}\,(3-\sigma)}z^2,$$

$$v = 0, \qquad w = \frac{(1+\sigma)\,\sigma w}{(3-\sigma)\,\mathrm{E}}xz,$$

and the corresponding stress components are easily shown to be

$$\mathrm{X}_x = -\frac{wx}{3-\sigma}, \qquad \mathrm{Y}_z = 0,$$

$$\mathrm{Y}_y = -\frac{\sigma wx}{3-\sigma}, \qquad \mathrm{Z}_x = 0,$$

$$\mathrm{Z}_z = 0, \qquad \mathrm{X}_y = -\frac{(1-\sigma)\,wy}{2(3-\sigma)},$$

which give the correct body force, and so all the conditions are satisfied.

The displacement at the centre is given by

$$u = \frac{(1-\sigma^2)\,wb^2}{2\mathrm{E}(3-\sigma)} = \frac{\mathrm{W}\,(-\sigma^2)}{4\pi\,(3-\sigma)\,\mathrm{E}h}.$$

This displacement is entirely in the plane of the plate and is small compared with the displacement in the direction normal to the plate, when it is horizontal, for in the latter case there is a term involving h^3 in the denominator.

(3) For the case in which the disc is held vertically in a groove at the rim in such a manner that the normal displacements there are zero, but tangential displacements are possible, the boundary conditions are that the normal displacement and the tangential stress resultant S must vanish at the rim.

Our previous solutions cannot be combined in any manner so as to satisfy these conditions. We can obtain another solution for the case in which there are no body forces in the following way:—

We may express the stress components in terms of a function ψ, which satisfies $\nabla^4\psi = 0$, in the form

$$\widehat{rr} = \frac{1}{r^2}\cdot\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{r}\cdot\frac{\partial\psi}{\partial r}, \qquad \widehat{\theta\theta} = \frac{\partial^2\psi}{\partial r^2}, \qquad \widehat{\theta r} = \frac{-\partial}{\partial r}\left(\frac{1}{r}\cdot\frac{\partial\psi}{\partial r}\right).$$

We try a solution

$$\psi = \mathrm{A}r^3\cos\theta + (\mathrm{B}r^3 + \mathrm{C}r^5)\cos 3\theta,$$

and then we have

$$\widehat{rr} = 2\mathrm{A}r\cos\theta - (6\mathrm{B}r + 4\mathrm{C}r^3)\cos 3\theta = (\mathrm{X}_x\cos^2\theta + \mathrm{Y}_y\sin^2\theta + \mathrm{X}_y\sin 2\theta),$$
$$\widehat{\theta\theta} = 6\mathrm{A}r\cos\theta + (6\mathrm{B}r + 20\mathrm{C}r^3)\cos 3\theta = (\mathrm{X}_x\sin^2\theta + \mathrm{Y}_y\cos^2\theta - \mathrm{X}_y\sin 2\theta),$$
$$\widehat{\theta r} = 2\mathrm{A}r\sin\theta + (6\mathrm{B}r + 12\mathrm{C}r^3)\sin 3\theta = [\tfrac{1}{2}(\mathrm{Y}_y - \mathrm{X}_x)\sin 2\theta + \mathrm{X}_y\cos 2\theta],$$
$$\therefore\quad 2\mathrm{A}r\cos\theta + (6\mathrm{B}r + 12\mathrm{C}r^3)\cos 3\theta = [\tfrac{1}{2}(\mathrm{Y}_y - \mathrm{X}_x)\cos 2\theta - \mathrm{X}_y\sin 2\theta],$$

whence we deduce that

$$\mathrm{X}_x = 2(\mathrm{A} - 3\mathrm{B})x - 4\mathrm{C}x(x^2 + 9y^2),$$
$$\mathrm{Y}_y = 6(\mathrm{A} + \mathrm{B})x + 4\mathrm{C}x(5x^2 - 3y^2),$$
$$\mathrm{Y}_x = -2(\mathrm{A} - 3\mathrm{B})y + 12\mathrm{C}y(x^2 + y^2),$$

whence

$$\frac{\partial u}{\partial x} = \frac{1}{\mathrm{E}}\{[2\mathrm{A} - 6\mathrm{B} - 6\sigma(\mathrm{A} + \mathrm{B})]x - 4\mathrm{C}(1 + 5\sigma)x^3 - 4\mathrm{C}(9 - 3\sigma)xy^2\},$$

$$\frac{\partial v}{\partial y} = \frac{1}{\mathrm{E}}\{[6(\mathrm{A} + \mathrm{B}) - 2\sigma(\mathrm{A} - 3\mathrm{B})]x + 4\mathrm{C}(5 + \sigma)x^3 - 4\mathrm{C}(3 - 9\sigma)xy^2\},$$

$$\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} = \frac{2(1 + \sigma)}{\mathrm{E}}\{2(3\mathrm{B} - \mathrm{A})y + 12\mathrm{C}y(x^2 + y^2)\}.$$

These three equations are satisfied by

$$u = \frac{1}{\mathrm{E}}[\{(1 - 3\sigma)\mathrm{A} - 3(1 + \sigma)\mathrm{B}\}x^2 - \{(5 + \sigma)\mathrm{A} - 3(1 + \sigma)\mathrm{B}\}y^2 - \mathrm{C}(1 + 5\sigma)x^4$$
$$- 2\mathrm{C}(9 - 3\sigma)x^2y^2 + (7 + 3\sigma)\mathrm{C}y^4 + \mathrm{D}],$$

$$v = \frac{1}{\mathrm{E}}[\{(6 - 2\sigma)\mathrm{A} + 6(1 + \sigma)\mathrm{B}\}xy + 4\mathrm{C}(5 + \sigma)x^3y - 4\mathrm{C}(1 - 3\sigma)xy^3].$$

The normal component of the displacement at any point is $(ux + vy)/r$

$$= \frac{x}{r\mathrm{E}}[\{(1 - 3\sigma)\mathrm{A} - 3(1 + \sigma)\mathrm{B}\}x^2 + \{(1 - 3\sigma)\mathrm{A} + 9(1 + \sigma)\mathrm{B}\}y^2$$
$$- \mathrm{C}(1 + 5\sigma)(x^2 + y^2)(x^2 - 3y^2) + \mathrm{D}].$$

$$\mathrm{S} = 2h\left[2\mathrm{A}y + \left(\frac{6\mathrm{B}}{r^2} + 12\mathrm{C}\right)\{3y(x^2 + y^2) - 4y^3\}\right].$$

We combine this solution with the solution (α) above, for which the normal displacement at any point is

$$\frac{w(1 + \sigma)}{4\mathrm{E}} \cdot \frac{x}{r}(y^2 - x^2).$$

Then, when $r = b$, by putting $x^2 = b^2 - y^2$, and equating the coefficients of x, x^3 to zero, we obtain

$$\mathrm{A} = -\frac{w}{4}, \quad \mathrm{B} = -\frac{w(1 + \sigma)}{4(5 + \sigma)}, \quad \mathrm{C} = \frac{w(1 + \sigma)}{8b^2(5 + \sigma)}, \quad \mathrm{D} = \frac{wb^2(3 - 5\sigma)}{8},$$

so that the components of displacement at any point of the disc are given by

$$u = \frac{w}{8\mathrm{E}(5+\sigma)b^2}\{4(3\sigma^2+10\sigma-1)b^2x^2+4(11+2\sigma-\sigma^2)b^2y^2$$
$$-(1+\sigma)(1+5\sigma)x^4-6(3-\sigma)(1+\sigma)x^2y^2+(7+3\sigma)(1+\sigma)y^4\}$$
$$+\frac{wb^2}{8\mathrm{E}}(3-5\sigma).$$

$$v = -\frac{w}{\mathrm{E}(5+\sigma)}\cdot\frac{xy}{b^2}\left\{(9+2\sigma+\sigma^2)b^2-\{(5+\sigma)x^2-(1-3\sigma)y^2\}\frac{1+\sigma}{2}\right\},$$

The central deflection is given by

$$u = \frac{wa^2}{8\mathrm{E}}(3-5\sigma) = \frac{\mathrm{W}}{16\pi\mathrm{E}h}(3-5\sigma), \qquad v = 0.$$

In the case in which the plate is inclined to the vertical there will be a superposition of the two effects. There is now a component of gravity in the plane of the plate and a component normal to it. This produces the normal sag which is, in general, the chief distortion. The component of the force in the plane of the plate produces small displacements in the plane, accompanied by very slight normal displacements, which are symmetrical about and vanish on the central plane.

We can obtain some information as to the relative magnitudes of these effects from the results which have been already obtained.

When the plate is supported horizontally at the centre it has been shown that the deflection at the edge is

$$\frac{3\mathrm{W}b^2}{128\pi\mathrm{E}h^3}(1-\sigma)(7+3\sigma)-\frac{\mathrm{W}}{40\pi\mathrm{E}h}(24+\sigma).$$

The ratio of the two terms which occur in this expression is

$$\frac{16}{15}\cdot\frac{24+\sigma}{(1-\sigma)(7+3\sigma)}\cdot\frac{h^2}{b^2}.$$

If we put $\sigma = \frac{1}{4}$, and $h = \frac{1}{10}b$, which gives ratio of aperture : thickness equal to 10, we obtain ratio of the two terms to be 1 : 22·5, so that the second term is tolerably small when compared with the first.

When the plate is supported at the rim the deflection at the centre is

$$\frac{3\mathrm{W}b^2}{128\pi\mathrm{E}h^3}(1-\sigma)(5+\sigma)+\frac{\mathrm{W}}{640\pi\mathrm{E}h}(87+79\sigma+24\sigma^2),$$

and the ratio of the second term in this expression to the first under the same conditions is 1 : 54·5.

In the case in which the plate was held vertically and clamped at the edge we have seen that the central displacement is

$$\frac{W(1-\sigma^2)}{4\pi(3-\sigma)Eh},$$

and the ratio of this to the small term $(24+\sigma)W/40\pi Eh$ occurring in the normal displacement when supported at the centre is

$$\frac{1-\sigma^2}{10(3-\sigma)(24+\sigma)} = \frac{1}{711},$$

and so is very small indeed. The displacement in the plane of the disc when this is held vertical is in this case only about 1/16,000 of the normal displacement at the edge when the disc is supported horizontally at the centre.

If the disc is vertical and held at the centre the relative displacement for points on the same radius at distances r_1, r_2 from the centre is

$$u_1-u_2 = \frac{W(1+\sigma)}{16\pi Ehb^2}\{-3(1-\sigma)(r_1^2-r_2^2)\cos^2\theta+(3+\sigma)(r_1^2-r_2^2)\sin^2\theta\} + \frac{W}{8\pi Eh}(3-\sigma)(1+\sigma)\log\frac{r_1}{r_2}.$$

If $r_1 = b = 50$ cm. and $r_2 = 1$ cm., then $u_{50}-u_1$ has a maximum value when $\theta = \frac{1}{2}\pi$, and this maximum is approximately

$$\frac{W(1+\sigma)}{16\pi Eh}(3+\sigma)+\frac{W}{8\pi Eh}(3-\sigma)(1+\sigma)\log_e 50 = \frac{W}{16\pi Eh}\,29{\cdot}3,$$

which is rather larger than the small term $W(24+\sigma)/40\pi Eh$ which occurs in **W** in the first horizontal case considered.

When the disc was vertical and supported round the rim the central deflection was $W(3-5\sigma)/16\pi Eh$. This is about 5/4 the value when the edge is clamped.

It follows that, unless the disc when horizontal is very well supported at the back, the displacement normal to the disc which is produced by its weight is very large compared with the displacement in the plane of the disc when it is held vertically.

We have now to apply the results which have been obtained to discuss the extent to which resolving power is affected by the flexure. We suppose the undistorted mirror to be accurately paraboloidal with a focal length a, and take a system of rectangular axes such that the z axis is the axis of the mirror, and the vertex is at the origin. Then the equation of the paraboloid is

$$x^2+y^2 = 4az.$$

A bundle of rays all parallel to the axis will after reflection all pass through the point of intersection of the axis with the focal plane, *i.e.* through the point $x = 0$, $y = 0$, $z = a$.

We consider now another parallel bundle, each ray of which makes a small angle θ with the axis. The ray which passes through the point (α, β, γ) of the surface has the equation

$$\frac{x-\alpha}{\theta} = \frac{y-\beta}{0} = \frac{z-\gamma}{1}.$$

Then the reflected ray may be represented by

$$\frac{x-\alpha}{l} = \frac{y-\beta}{m} = \frac{z-\gamma}{n}.$$

Since the direction cosines of the normal to the surface are proportional to α, β, $-2a$, and since the incident and reflected rays make equal angles with the normal, and are all in the same plane, we have the conditions

$$l\alpha + m\beta - n \,.\, 2a = \alpha\theta - 2a;$$

and also

$$\begin{vmatrix} l & m & n \\ \alpha & \beta & -2a \\ \theta & 0 & 1 \end{vmatrix} = 0,$$

together with

$$l^2 + m^2 + n^2 = 1.$$

Since θ has been assumed so small that its square and higher powers may be neglected, and since also

$$\alpha^2 + \beta^2 = 4a\gamma,$$

we obtain for the values of l, m, n the expressions, correct up to terms including θ,

$$l = -\frac{\alpha}{a+\gamma} + \left\{\frac{\alpha^2}{2a(a+\gamma)} - 1\right\}\theta, \qquad m = -\frac{\beta}{a+\gamma} + \frac{\alpha\beta}{2a(a+\gamma)}\theta$$

$$n = \frac{a-\gamma}{a+\gamma} - \frac{\alpha\theta}{a+\gamma},$$

and, to the same order of approximation, the co-ordinates of the point in which the reflected ray cuts the focal plane are given by

$$x = -\frac{\theta}{2a} \cdot \frac{a+\gamma}{a-\gamma}(2a^2 + \alpha^2 - 2a\gamma), \qquad y = -\frac{\theta}{2a} \cdot \frac{a+\gamma}{a-\gamma}\alpha\beta,$$

or the distance from the axis of the point in which the reflected ray through (α, β, γ) cuts the focal plane is

$$\theta\left(\frac{a+\gamma}{a-\gamma}\right)\{(a+\gamma)^2 - \beta^2\}^{\frac{1}{2}}.$$

For a given value of γ this is greatest when $\beta = 0$, *i.e.* for the point in the

plane through the axis which contains the direction of the bundle. For points in this plane the greatest value is at the edge, and is $\theta(a+\gamma_e)^2/(a-\gamma_e)$ where γ_e is the edge value.

Since even for points on the rim γ_e will be comparatively small we may take this distance to be approximately $a\theta$.

Now two points of light, one of which is on the axis and the other at a small angular distance θ, will be resolved provided that $\theta \geq 0{\cdot}61\,\lambda/b$, where λ is the wave-length of the light, and b is the semi-aperture of the telescope, for when this condition is satisfied the angular separation of the spots is of sufficient magnitude to prevent their first diffraction maxima overlapping.

Hence if two stars are to appear distinct, the breadth of the central image for parallel rays must not exceed $0{\cdot}61\lambda a/b$.

Suppose now that the undistorted surface has for its equation

$$\xi^2+\eta^2 = 4a\zeta.$$

Then u, v, w, the components of the displacement of the point ξ, η, ζ, are functions of ξ and η, and the co-ordinates of the displaced point are given by

$$x = \xi+u, \qquad y = \eta+v, \qquad z = \zeta+w.$$

Since u, v, w are all small we can in them put $\xi = x$, $\eta = y$, so that they become functions of x and y. The equation of the deformed surface is therefore

$$(x-u)^2+(y-v)^2 = 4a(z-w).$$

We consider first, for simplicity, the deformation which is produced when the disc is horizontal. In this case $u = v = 0$, the only displacement being normal to the disc and symmetrical, so that we can proceed in two dimensions.

The section of the surface by the xz plane has for its equation

$$x^2 = 4a(z-w).$$

The equation of an incident ray parallel to the axis is $x = \alpha$, and since the direction cosines of the normal to the surface at the point α are proportional to

$$\alpha+2a\left(\frac{\partial w}{\partial x}\right)_\alpha, \qquad -2a,$$

it follows that, the reflected ray being

$$\frac{x-\alpha}{l} = \frac{z-\gamma}{n},$$

l and n are given by the equations

$$l = -4a\left(\alpha+2a\frac{\partial w}{\partial x_\alpha}\right)\Big/\left\{4a^2+\left(\alpha+2a\frac{\partial w}{\partial x_\alpha}\right)^2\right\},$$

$$n = \left\{4a^2-\left(\alpha+2a\frac{\partial w}{\partial x_\alpha}\right)^2\right\}\Big/\left\{4a^2+\left(\alpha+2a\frac{\partial w}{\partial x_\alpha}\right)^2\right\},$$

and the reflected ray is

$$x = \alpha - \frac{4a\left(\alpha + 2a\dfrac{\partial w}{\partial x_\alpha}\right)}{4a^2 - \left(\alpha + 2a\dfrac{\partial w}{\partial x_\alpha}\right)^2}\left\{z - \frac{\alpha^2 + 4aw}{4a}\right\}.$$

If $w = 0$, *i.e.* if the mirror is undistorted, there is perfect focussing at $z = a$. We suppose then that the nearest approach to focussing when the mirror is bent is on the plane $z = a + \zeta$, where ζ is a small quantity which has to be determined.

Then the corresponding value of x is given by

$$x = \alpha - \frac{4a(\alpha + 2aw_\alpha)}{4a^2 - \alpha^2 - 4a\alpha w_\alpha}\left\{\frac{4a^2 - \alpha^2 + 4a(\zeta - w)}{4a}\right\},$$

where w_α has been used to denote $(\partial w/\partial x)_\alpha$, and where squares of w have been neglected.

On expansion, retaining only first power of w, there results

$$x = -2aw_\alpha - \frac{4a\alpha(\alpha w_\alpha + \zeta - w)}{4a^2 - \alpha^2}.$$

(1) In the case when the disc is clamped at the edge it has been shown that

$$w = k(b^2 - x^2)^2, \quad \text{where} \quad k = \mathrm{W}/64\pi b^2\mathrm{D}.$$

By differentiation of the above value of x it is found that the condition for a stationary intercept is

$$2(\alpha w_\alpha + \zeta - w) + (4a^2 - \alpha^2)\,w_{\alpha\alpha} = 0,$$

where $w_{\alpha\alpha} = (\partial^2 w/\partial x^2)_\alpha$, and then we get

$$x = 2a(\alpha w_{\alpha\alpha} - w_\alpha).$$

The condition for a stationary value becomes in the case at present under discussion,

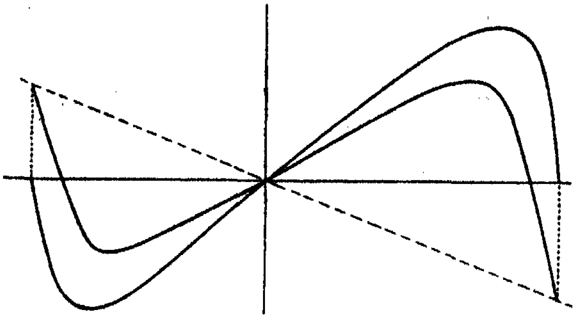
$$3\alpha^4 - 24a^2\alpha^2 + b^2(b^2 + 8a^2) - \zeta/k = 0.$$

For a given value of ζ there are two values of α. In the case in which $\zeta = kb^2(8a^2 + b^2)$, these combine to give an inflexional tangent at $\alpha = 0$.

The value of x at any point is

$$x = \frac{k\alpha}{a}\left\{(8a^2 + b^2 + 3\alpha^2)(b^2 - \alpha^2) - \frac{\zeta}{k}\right\}.$$

The part which is independent of ζ vanishes at the two edges, $\alpha = \pm b$, and the two parts add as shown in the diagram.



The position of the stationary points depends upon the value assigned to ζ, and the values at the ends may be either greater or less than the maxima. The most favourable case, giving the least breadth, will occur when the two are equal.

Retaining only the most important terms the maxima are given by

$$8a^2(b^2-3\alpha^2) = \zeta/k,$$

and to the same order are equal to $16ka\alpha^3$.

The end values when $\alpha = b$ are equal to $b\zeta/a$.

Hence the condition that this is equal to the maximum is

$$\frac{b\zeta}{16ka^2} = \left\{\frac{b^2}{3} - \frac{\zeta}{24ka^2}\right\}^{\frac{3}{2}},$$

which is satisfied by $\zeta = 2ka^2b^2$, giving a breadth of image $2b\zeta/a$, equal to $4kab^3$, and this gives the limiting condition that

$$4kab^3 < 0{\cdot}61\lambda a/b.$$

The following approximate mean values for glass are sufficient to determine the magnitude of the permissible limits for b, viz.:—

$$\rho = 3, \qquad \mathrm{E} = 6\times10^{11}\ \text{C.G.S. units}, \qquad \lambda = 6\times10^{-5}\ \text{cm.},$$

and

$$k = 3g\rho(1-\sigma^2)/64\mathrm{E}h^3.$$

Putting $\sigma = \frac{1}{4}$, the condition is that

$$\frac{b^4}{h^3} < \frac{3\mathrm{E}\lambda}{g\rho}\left(\frac{16}{15}\right)^2, \quad \text{or} \quad b^2 < 204{\cdot}3\,h.$$

If the mirror is so constructed that $h = \frac{1}{10}b$, then the limiting value of b is 20·4 cm., and so in this case the resolving power is lost for a very small breadth of aperture. Since the limiting condition is $b^2/h =$ const. this result is also an example of the general law that the thicker the mirror the larger is the permissible breadth of the aperture.

In the case when the disc is horizontal and supported at the edge, the value of w was found to be

$$w = \frac{W}{64\pi a^3 D}(b^2-r^2)\left(\frac{5+\sigma}{1+\sigma}b^2-r^2\right) = k(b^2-r^2)(\gamma b^2-r^2) \quad \text{(say)},$$

where k has the same value as above.

Proceeding exactly as above it is easily found that the stationary values are given by

$$4a^2\{(\gamma+1)b^2-6\alpha^2\} = \zeta/k:$$

and when $\alpha = b$,

$$x = \frac{kb}{a}\{4(\gamma-1)a^2b^2\}-\frac{b\zeta}{a}.$$

The maxima and minima are again $= 16ka\alpha^3$, and so the condition that these are equal to the end values is

$$16ka\alpha^3 = 16ka\left\{\frac{(\gamma+1)b^2}{6}-\frac{\zeta}{24ka^2}\right\}^{\frac{3}{2}} = 4k(\gamma-1)ab^3-\frac{b\zeta}{a},$$

which is satisfied by $\zeta = 2(2\gamma-1)ka^2b^2$, giving a breadth equal to $4kab^3$ exactly as before, and so—since k has the same value—the limiting value of b in order that the resolving power may still increase with increase of aperture has the same value as before.

(2) Coming now to the next case considered, in which the plate was supported both at the centre and at the edge, the value of W was shown to be

$$\mathsf{W} = kr^4+\frac{A}{4}r^2(\log r-1)+\frac{Br^2}{4},$$

where A, B were determined, and here $r = x$.

Then the intercept on the plane $z = a+\zeta$ is

$$x = -2a\frac{w_\alpha(4a^2+\alpha^2)+2a(\zeta-w)}{4a^2-\alpha^2-4a\alpha w_\alpha}$$

$$= -2a\alpha\left[4k\alpha^2+\frac{A}{2}(\log\alpha-\tfrac{1}{2})+\frac{B}{2}+\frac{1}{4a^2}\left(6k\alpha^4+\frac{A}{2}\alpha^2\log\alpha+\frac{B\alpha^2}{2}\right)+\frac{\zeta}{2a^2}\right],$$

approximately, neglecting all terms of higher order.

The maximum value of the intercept is determined by the condition

$$12k\alpha^2+\frac{A}{2}(\log\alpha+\tfrac{1}{2})+\frac{B}{2}+\frac{\zeta}{2a^2}+\frac{1}{4a^2}\left\{30k\alpha^4+\frac{A}{2}(3\alpha^2\log\alpha+\alpha^2)+\frac{3B\alpha^2}{2}\right\} = 0,$$

and for this value of α,

$$x = a\left[16k\alpha^3+A\alpha+12k\frac{\alpha^5}{a^2}+\frac{A}{4a^2}(2\log\alpha+1)\alpha^3+\frac{B\alpha^3}{2a^2}\right].$$

If we adjust so that the maximum and the value at the edge are equal and

opposite, then the images from the two halves of the mirror overlap. This requires that

$$16k\alpha^3+A\alpha+12k\frac{\alpha^5}{a^2}+\frac{A}{4a^2}(2\log\alpha+1)\alpha^3+\frac{B\alpha^3}{2a^2}$$
$$=2b\left[4kb^2+\frac{A}{2}(\log b-\tfrac{1}{2})+\frac{1}{4a^2}\left(6kb^4+\frac{A}{2}b^2\log b+\frac{Bb^2}{2}\right)-12k\alpha^2\right.$$
$$\left.-\frac{A}{2}(\log\alpha+\tfrac{1}{2})-\frac{1}{4a^2}\left(30kb^4+\frac{A}{2}b^2(3\log b+1)+\frac{3Bb^2}{2}\right)\right],$$

where the value of ζ determined by the maximum condition has been used.

Since the focal length is usually about five times the aperture, *i.e.* $a = 10b$, the ratio of the terms $6kb^4/4a^2$, $4kb^2$ is $\frac{3}{8}\frac{b^2}{a^2}=\frac{3}{800}$, and so very little error will be caused by working with the approximate first terms.

Then for the determination of the value of α at the maximum we have the equation

$$16k\alpha^3+A\alpha = 2b\left\{4kb^2-12k\alpha^2+\frac{A}{2}\left(\log\frac{b}{\alpha}-1\right)\right\}.$$

Now $$\frac{A}{k}=-\frac{5+\sigma}{3+\sigma}8b^2=-\frac{168}{13}b^2=-13b^2, \text{ approx.},$$

so that $$16\alpha^3-13b^2\alpha+24\alpha^2b-21b^3=13b^3\log\alpha/b;$$

or, putting $\alpha=\lambda b$,

$$16\lambda^3+24\lambda^2-13\lambda-21=13\log\lambda.$$

By trial it is found that $\lambda=\frac{9}{10}$ nearly satisfies, so that we write

$$\lambda = 0{\cdot}9+\xi,$$

where ξ is small. A second approximation gives $\xi = 0{\cdot}004$, so that it is sufficiently accurate to take $\alpha=\frac{9}{10}b$ at the maximum.

Since the first terms are now comparatively small, we include also the next order terms on substitution of this value of α, and by writing $a = 10b$, and

$$\frac{B}{k}=-\frac{13+3\sigma-2(5+\sigma)\log b}{3+\sigma}4b^2=-\frac{55-42\log b}{13}4b^2,$$

it is found that the breadth of the image is $2(0{\cdot}053)kab^3$, and therefore the limiting condition is that

$$2(0{\cdot}053)kab^3<\tfrac{4}{3}\lambda a/b,$$

or, using the same values for the constants as before, this condition gives $b^2<1255h$, and if $h=\frac{1}{10}b$,

$$b<125{\cdot}5 \text{ cm., or } b<49{\cdot}4 \text{ inches},$$

and so the limiting permissible value of the radius, in this case, the thickness being $\frac{1}{10}$th of the aperture, is about 4 feet.

If we use a thicker plate we can use a mirror of larger aperture, *e.g.* if $h = \frac{1}{8}b$, then $b = 82$ inches, or the permissible radius is nearly 7 feet.

By comparison with the preceding cases, it is at once apparent how great is the advantage which is obtained simply by supporting the mirror at the centre in addition to the edge.

(3) It now remains to discuss the last mode of support considered, when the disc was horizontal, viz., when it is supported at the centre, round the circumference, and round a concentric circle of radius c. Using the values of the displacement which were found for the two portions of the disc we obtain for the values of the intercept on the plane $z = a+\zeta$ the values, according as $\alpha < c$ or $> c$ respectively,

$$x_1 = -2a\alpha \left\{ 4k\alpha^2 + 2\mathrm{A}'(\log\alpha - \tfrac{1}{2}) + 2\mathrm{B}' + \frac{\mathrm{C}'}{c^2} - 2\frac{\mathrm{C}'}{c^2}\log\frac{\alpha}{c} \right.$$
$$\left. + \frac{1}{2a^2}\left(3k\alpha^4 + \mathrm{A}'\alpha^2\log\alpha + \mathrm{B}'\alpha^2 - \mathrm{C}'\frac{\alpha^2}{c^2}\log\frac{\alpha}{c}\right) + \frac{\zeta'}{2a^2} \right\},$$

$$x_2 = -2a\alpha \left\{ 4k\alpha^2 + 2\mathrm{A}'(\log\alpha - \tfrac{1}{2}) + 2\mathrm{B}' + \frac{\mathrm{C}'}{\alpha^2} \right.$$
$$\left. + \frac{1}{2a^2}\left(3k\alpha^4 + \mathrm{A}'\alpha^2\log\alpha + \mathrm{B}'\alpha^2 - \mathrm{C}'\log\frac{\alpha}{c}\right) + \frac{\zeta'}{2a^2} \right\},$$

which are continuous at $\alpha = c$, as they should be.

We can abbreviate the work and at the same time illustrate the advantage given by the additional support if we take a special value for c. The simplest value to take is $c = b/2$, and then, by putting $\sigma = \frac{1}{4}$, we have A′, C′ given by

$$\mathrm{A}' = -4{\cdot}273\,kb^2, \qquad \mathrm{C}' = -1{\cdot}01\,kb^4,$$

and also
$$\mathrm{B}' = -\mathrm{A}'\log b - 3{\cdot}196\,kb^2.$$

On investigation, it is found that the conditions cannot be satisfied by supposing the maximum deflection to fall in the inner portion, and by making it equal to the end deflection. We therefore make the maximum in the outer portion equal to the end deflection.

The condition for the maximum is

$$12k\alpha^2 + \mathrm{A}'(2\log\alpha + 1) + 2\mathrm{B}' - \frac{\mathrm{C}'}{\alpha^2} + \frac{\zeta}{2a^2} = 0,$$

and the corresponding maximum is

$$2a\alpha\left[8k\alpha^2 + 2\mathrm{A}' - \frac{2\mathrm{C}'}{\alpha^2}\right],$$

and the equation to determine α is

$$2a\alpha\left(8k\alpha^2+2A'-\frac{2C'}{\alpha^2}\right)=2ab\left[4kb^2+2A'(\log b-\tfrac{1}{2})+\frac{C'}{b^2}-12k\alpha^2\right.$$
$$\left.-A'(2\log\alpha+1)+\frac{C'}{\alpha^2}\right].$$

On substitution of the numerical values, we get

$$\frac{1\cdot 01}{\lambda^2}+\frac{2\cdot 02}{\lambda}+8\lambda^3+12\lambda^2-8\cdot 546\lambda-11\cdot 53=8\cdot 546\log_e\lambda=19\cdot 678\log_{10}\lambda.$$

By trial it is found that $\lambda = 0\cdot 6$ nearly satisfies, and by substituting $\lambda = 0\cdot 6+\xi$, and retaining first powers only of ξ, a nearer approximation is $\lambda = 0\cdot 593$. Including now the next order terms the total breadth of the image is found to be $4akb^3(0\cdot 004)$, and the limiting condition is that $0\cdot 16\times\frac{3g\rho}{64Eh^2}\times b^3<\frac{3}{8}\lambda b$, so that $b^2<3128h$, or $b<312\cdot 8$ cm. <123 inches, if $h=\frac{1}{10}b$.

The limiting value of the radius of the mirror is thus increased to about 10 feet, as compared with the 4-foot radius obtained in the case in which the support at half the radial distance is absent.

The cases which have now been discussed are sufficient to enable us to conclude that as far as the displacement normal to the plane of the disc, produced by the component of gravity in that direction, is concerned, the effect on the resolving power may be practically nullified if care is taken to support the mirror well at the back. Although the methods of support considered above are necessarily somewhat ideal, it is certain that with a mirror well supported at the back, as *e.g.* is the case in the method devised by Ritchey for the large reflecting telescope at Mount Wilson Observatory, it is possible to use mirrors of an aperture which is far beyond the limits which at present are practically attainable.

This discussion has also shown how, for a given mode of support, larger apertures may be used provided that the thickness of the mirror is increased sufficiently. The thickness to be used must of course be determined by practical considerations, such as the possibility of obtaining a homogeneous mirror, or by the question of the weight which the supports are designed to bear.

For the remainder of the discussion we shall suppose the mirror to be well enough supported at the back for the normal component of gravity to have no effect upon the resolving power, so that it only remains to discuss the effect of the displacements which occur in the plane of the disc. We will

therefore consider the case in which the disc is vertical, as then these displacements will have their maximum value. The nature of the back support does not now concern us, and whatever this may be the disc must also be held in some manner at the edge and it will be impossible to prevent the displacement in the plane of the disc from taking place.

Putting $w = 0$, the equation of the mirror becomes

$$x^2+y^2-2xu-2yv = 4az.$$

The equation of the normal at (α, β, γ) is

$$\frac{x-\alpha}{p} = \frac{y-\beta}{q} = \frac{z-\gamma}{2a}\,.$$

where $\qquad -p = \alpha-u-\alpha u_\alpha-\beta v_\alpha \qquad -q = \beta-v-\beta v_\beta-\alpha u_\beta,$

and it is easily shown that corresponding to a ray incident at the point (α, β, γ) of the surface parallel to the axis, the reflected ray is

$$\frac{x-\alpha}{l} = \frac{y-\beta}{m} = \frac{z-\gamma}{n},$$

where l, m, n are given by

$$l = \frac{4ap}{4a^2+p^2+q^2}, \qquad m = \frac{4aq}{4a^2+p^2+q^2}, \qquad n = \frac{4a^2-p^2-q^2}{4a^2+p^2+q^2};$$

and as far as the first order only in the displacements, by substituting for γ, p, q in terms of α, β, u, v, and putting $z = a+\zeta$, we have

$$x = u+\frac{(4a^2+\alpha^2-\beta^2)(\alpha u_\alpha+\beta v_\alpha)+2\alpha\beta(\beta v_\beta+\alpha u_\beta)-4a\alpha\zeta}{4a^2-\alpha^2-\beta^2};$$

and, similarly,

$$y = v+\frac{(4a^2+\beta^2-\alpha^2)(\beta v_\beta+\alpha u_\beta)+2\alpha\beta(\alpha u_\alpha+\beta v_\alpha)-4a\beta\zeta}{4a^2-\alpha^2-\beta^2}.$$

For simplicity of discussion, we will consider first the case in which $\beta = 0$, *i.e.* we consider for the present only the rays which are incident at points on the mirror in the vertical plane through its axis.

For the case of the mirror which is clamped at the edge

$$u = k(b^2-\alpha^2), \qquad v = 0,$$

where
$$k = \frac{W(1-\sigma^2)}{4\pi Eh(3-\sigma)b^2} = \frac{(1-\sigma^2)g\rho}{2E(3-\sigma)},$$

and so
$$y = 0, \quad \text{and} \quad x = k(b^2-\alpha^2)-\frac{4a^2+\alpha^2}{4a^2-\alpha^2}2k\alpha^2-\frac{4a\alpha\zeta}{4a^2-\alpha^2}$$

$$= k(b^2-3\alpha^2)-\frac{4\alpha\zeta}{a}.$$

Neglecting the term in α^4/a^2 and all terms of a higher order, we see that, for a given value of ζ, x is a maximum when $\alpha = -2\zeta/3ak$.

We suppose that ζ is positive: then the intercept x is positive and is equal to $kb^2+\frac{4}{3}\zeta^2/a^2k^2$.

The value of x steadily diminishes with increase of α, since ζ is supposed positive, and so the greatest negative intercept is from $\alpha=b$ and is $-2kb^2-4b\zeta/a$, so that the total breadth of the band is

$$3kb^2+\frac{4b\zeta}{a}+\frac{4\zeta^2}{3ka^2}=\frac{(2\zeta+3akb)^2}{3ka^2},$$

and to this order is least when we put $\zeta=0$.

A similar result is obtained if ζ is supposed negative, since then the greatest negative intercept is from $\alpha=-b$.

Thus the least value of the intercept on a plane perpendicular to the axis produced by the reflection of a beam incident parallel to the axis in the vertical plane through the axis is $3kb^2$. The upper limit for b in order that the resolving power may not decrease with increase of the size of the mirror is given by

$$3kb^2<\tfrac{4}{3}\lambda a/b \quad \text{or} \quad b^3/a<\tfrac{4}{3}E\lambda(3-\sigma)/(1-\sigma^2)g\rho,$$

and if the focal length is five times the aperture, $a=10b$, we obtain the limiting value of b to be

$$b=379 \text{ cm.}=149 \text{ inches},$$

and so the limiting radius of the mirror is about 12·5 feet, and quite a large size is permissible.

Whereas, in the cases previously considered in which the mirror was horizontal, the determining factor was the ratio of the aperture of the mirror to its thickness, the limiting value of the radius being found from an equation of the type $b^2/h=$ constant; in the present case the determining factor is the ratio of the aperture to the focal length, the limiting value of b being found from an equation of the type $b^3/a=$ constant.

If it was desired to construct a mirror of given focal length and of as large an aperture as possible, the limit for the aperture could be determined from the above. Thus, if the required focal length were 50 feet, the largest radius which may be used is 280 cm., or about 9 feet.

In the more general case when β is not zero we have for a first approximation

$$x=u+\alpha u_\alpha+\beta v_\alpha, \qquad y=v+\beta v_\beta+\alpha u_\beta.$$

Or, since $$u=k(b^2-\alpha^2-\beta^2), \quad v=0,$$

we have $$x=k(b^2-3\alpha^2-\beta^2), \qquad y=-2k\alpha\beta.$$

Corresponding to the centre $\alpha=\beta=0$, we have $x=kb^2$, $y=0$, and the radius vector from this point to any other point of the patch is given by

$$k\{(\alpha^2+\beta^2)^2+8\alpha^2(\alpha^2+\beta^2)\}^{\frac{1}{2}},$$

and this attains its greatest value when $(\alpha^2+\beta^2)$ and α^2 have their greatest values, *i.e.* at the two points on the circumference in the vertical plane through the axis, and then $\rho = 3kb^2$. This gives the maximum extent of the swing for light incident at any point, and is the case discussed above.

In the other case considered, in which the normal component of the displacement at any point of the edge vanishes, the normal component of the displacement at any point of the disc, using the values of u, v, previously obtained, is given by

$$\frac{\alpha u+\beta v}{\rho} = \frac{w\alpha}{(5+\sigma)\,\mathrm{E}\rho}\left\{\tfrac{1}{2}(3\sigma^2+10\sigma-1)\,\alpha^2-\tfrac{1}{2}(3\sigma^2+2\sigma+7)\,\beta^2 \right.$$
$$\left. -\frac{1}{8b^2}(1+\sigma)(1+5\sigma)(\alpha^2+\beta^2)(\alpha^2-3\beta^2)\right\}$$
$$+\frac{w\alpha}{4\mathrm{E}\rho}\{(1+\sigma)(\beta^2-\alpha^2)+\tfrac{1}{2}b^2(3-5\sigma)\}.$$

The point in which the reflected ray from α, β cuts the focal plane is given by

$$x = u+\alpha u_\alpha+\beta v_\alpha, \qquad y = v+\beta v_\beta+\alpha u_\beta,$$

giving a normal component of amount

$$\frac{x\alpha+y\beta}{\rho} = \frac{u\alpha+v\beta}{\rho}+\alpha\left(\frac{\alpha}{\rho}\cdot\frac{\partial u}{\partial\alpha}+\frac{\beta}{\rho}\cdot\frac{\partial u}{\partial\beta}\right)+\beta\left(\frac{\alpha}{\rho}\cdot\frac{\partial v}{\partial\alpha}+\frac{\beta}{\rho}\cdot\frac{\partial v}{\partial\beta}\right),$$

and, since $\rho^2 = \alpha^2+\beta^2$, we obtain

$$\frac{\partial}{\partial\rho} = \frac{\alpha}{\rho}\cdot\frac{\partial}{\partial\alpha}+\frac{\beta}{\rho}\cdot\frac{\partial}{\partial\beta},$$

so that $$\frac{x\alpha+y\beta}{\rho} = \frac{u\alpha+v\beta}{\rho}+\alpha\frac{\partial u}{\partial\rho}+\beta\frac{\partial v}{\partial\rho} = \frac{\partial}{\partial\rho}(\alpha u+\beta v),$$

and so is given by

$$\frac{w}{\mathrm{E}(5+\sigma)}\cdot\frac{\partial}{\partial\rho}\left\{\frac{3\sigma^2+10\sigma-1}{2}\alpha^3-\frac{3\sigma^2+2\sigma+7}{2}\alpha\beta^2\right.$$
$$\left.-\frac{(1+\sigma)(1+5\sigma)}{8b^2}\alpha\rho^2(\alpha^2-3\beta^2)\right\}+\frac{\partial}{\partial\rho}\left\{\frac{w(1+\sigma)}{4\mathrm{E}}\alpha(\beta^2-\alpha^2)\right.$$
$$\left.+\frac{wb^2}{8\mathrm{E}}(3-5\sigma)\,\alpha\right\}$$
$$=\frac{w}{\mathrm{E}(5+\sigma)}\cdot\frac{\alpha}{\rho}\left\{\tfrac{3}{4}(5\sigma^2+14\sigma-7)\,\alpha^2-\tfrac{3}{4}(5\sigma^2-2\sigma+9)\,\beta^2\right.$$
$$\left.-\frac{(1+\sigma)(1+5\sigma)}{8b^2}5(\alpha^2+\beta^2)(\alpha^2-3\beta^2)+\frac{b^2}{8}(3-5\sigma)(5+\sigma)\right\}.$$

Or, putting $\alpha = \dfrac{\rho}{\sqrt{(1+\lambda^2)}}$, $\beta = \dfrac{\lambda\rho}{\sqrt{(1+\lambda^2)}}$, where λ is constant for a

definite radial direction, the normal component is

$$\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{\rho^2}{\sqrt{(1+\lambda^2)}} \left\{ \tfrac{3}{4}(5\sigma^2+14\sigma-7)\frac{1}{1+\lambda^2} - \tfrac{3}{4}(5\sigma^2-2\sigma+9)\frac{\lambda^2}{1+\lambda^2} \right.$$
$$\left. -\frac{(1+\sigma)(1+5\sigma)}{8b^2}\, 5\rho^2 \frac{1-3\lambda^2}{1+\lambda^2} + \frac{b^2}{8\rho^2}(5+\sigma)(3-5\sigma) \right\}.$$

The variation of this expression with ρ for a definite value of λ, *i.e.* along a definite radius, is

$$-\frac{w\rho}{\mathrm{E}(5+\sigma)b_2} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \tfrac{9}{32} \{17b^2+47\lambda^2 b^2+25(1-3\lambda^2)\rho^2\},$$

and the radial component of the intersection with the focal plane is found to be, on substitution for σ,

$$-\frac{w}{\mathrm{E}(5+\sigma)b^2} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \tfrac{9}{128} \{2(17+47\lambda^2)b^2\rho^2+25(1-3\lambda^2)\rho^4-\tfrac{49}{3}b^4\}.$$

There are two cases to be considered, according as $\lambda^2 \gtrless \frac{1}{3}$.

(α) If $\lambda^2 < \frac{1}{3}$, the radial intercept continually decreases with increase of ρ, so that the extreme values arise from the centre and circumference, and are

$$\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \tfrac{147}{128}\, b^2 \text{ at the centre}$$

and

$$-\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{1}{(1+\lambda^2)^{3/2}} (3+\tfrac{171}{128}\lambda^2)\, b^2 \text{ at the edge,}$$

and the maximum extent of the displacement is the difference of these, and is

$$\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \left(3+\frac{5\lambda^2}{2}\right) b^2,$$

very nearly.

This expression decreases with increase of λ and so has its maximum value when $\lambda = 0$, *i.e.* in the plane $\beta = 0$, and is then $3wb^2/\mathrm{E}(5+\sigma)$.

(β) If $\lambda^2 > \frac{1}{3}$, then the radial intercept has a stationary value for the value of ρ given by

$$\rho^2 = \frac{17+47\lambda^2}{25(3\lambda^2-1)} b^2,$$

and this value of ρ will be less than b provided that $\lambda^2 > \frac{3}{2}$.

Thus if $\lambda^2 < \frac{3}{2}$, the radial intercept continuously decreases from $\rho = 0$ to $\rho = b$. If, however, $\lambda^2 > \frac{3}{2}$ it reaches a minimum for a certain value of ρ which is less than b and is given by the above equation. After this it will commence to increase again, and the extreme values are at the centre and at this minimum.

For this value of ρ the intercept is

$$\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \cdot \frac{9b^2}{128} \left\{ -\frac{(17+47\lambda^2)^2}{25(3\lambda^2-1)} + \frac{49}{3} \right\},$$

and the maximum breadth of the image on the focal plane in the definite direction, λ, is

$$\frac{w}{\mathrm{E}(5+\sigma)} \cdot \frac{1}{(1+\lambda^2)^{3/2}} \cdot \frac{9b^2}{128} \cdot \frac{(17+47\lambda^2)^2}{25(3\lambda^2-1)}.$$

Considering now the variation of this expression with λ^2, as λ^2 increases from $\frac{3}{5}$ to ∞, we find that it continually decreases, and so has its greatest value when $\lambda^2 = \frac{3}{5}$, viz.,

$$\frac{225\sqrt{2}}{128\sqrt{5}} \cdot \frac{wb^2}{\mathrm{E}(5+\sigma)}.$$

This is less than the greatest value when $\lambda^2 < \frac{3}{5}$ and so the limiting condition for b is that

$$\frac{3wb^2}{\mathrm{E}(5+\sigma)} < \frac{3}{5}\frac{\lambda a}{b}, \quad \text{or} \quad \frac{b^3}{a} < \frac{21}{20}\frac{\lambda \mathrm{E}}{g\rho},$$

and on writing $a = 10b$ this gives a limiting value for b of 358 cm., or 141 inches, so that the disc may have with this mode of support a radius of nearly 12 feet.

This method of support corresponds closely to that used by Ritchey, who, in addition to the back support which prevented the normal displacements from being appreciable, placed the mirror in a circular metal band supported on the outside. In this way, there can be no normal displacements at the edge, but there is perfect freedom for tangential displacements to occur.

It has been assumed in the discussion immediately preceding that the mirror is held vertically. The displacements in this case necessarily attain their greatest possible values, and so if the radius is less than the critical value for this case, it will be so for any angle of inclination.

The results obtained in the present discussion may be briefly summarised as follows:—

1. The components of the displacement of any point of the mirror-disc arising from its weight have been calculated for various modes of support, both in the case when the mirror is held horizontally, and also when it is held vertically.

2. It is found that in all cases the displacements in the former case are very much larger than in the latter, and that if the mirror were not well supported at the back, the resolving power would begin to decrease as the aperture was increased for comparatively small breadths of aperture. The more complete is the back support, the larger of course is the critical size of mirror, and with simple forms of support this critical size is far larger than is likely to be practically reached.

3. It is also shown that for any given mode of support the critical size of the mirror may be increased by increasing at the same time its thickness.

4. When the mirror is held vertically the displacements are small, but the support cannot be so arranged as to get rid of them, as was the case with the normal component. It is shown, however, that the critical size of mirror is comparatively large, very much larger in fact than any mirrors at present in use, the limiting radius being somewhere in the neighbourhood of 12 feet in the two cases which are discussed in detail, when the telescope is so constructed that its focal length is five times its aperture and the aperture ten times the thickness of the mirror. For a given mode of support a larger aperture may be used by increasing the focal length.

On the Electrical Emissivity and Disintegration of Hot Metals.

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Introductory.

In February, 1912, the authors communicated to the Royal Society an account of some experiments on the emission of electricity from carbon at high temperatures.* In this investigation all the experiments were conducted at atmospheric pressure, and some evidence was brought forward that under these conditions the carriers of electricity appeared to consist almost wholly of "sputtered" matter, and that corpuscles—the carriers of negative electricity in high vacua—played in these experiments but a minor or at any rate an indirect part.

It was shown that, even in the absence of any applied potential, it was possible for charged particles to escape in sufficient number from a hot carbon surface to give rise, at high temperatures, to currents of ammeter rather than electrometer magnitude. The particles appeared to be emitted with considerable velocity and the emissivity of the radiating surface sending out the particles seemed to depend primarily on the temperature alone. It was, however, influenced to some degree also by the nature of the surrounding gas. Depending on this emissive property of carbon, a kind of ionic dynamo was constructed, capable of lighting intermittently a small group of glow-lamps (2 volts, 3 ampères).

* Harker and Kaye, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 379.

The general interest of these experiments, dealing with a high temperature phenomenon only as yet very imperfectly investigated, and, in addition, the incentive supplied by the recent interesting researches of Sir William Crookes,* on the volatility of metals of the platinum group, led us to undertake further experiments with a view to ascertaining to what extent the phenomena we had observed on a somewhat large scale with carbon could be reproduced with other substances.

A good deal of recent research has been devoted to the study of the question of the thermal sputtering of metals, but not much attention seems to have been paid by most of the observers to the accompanying electrical phenomena except in high vacua. It would appear also that of the experiments on metals at high temperatures, a very large proportion have been made on platinum, and, so far as we are aware, nearly all were carried out on a somewhat small scale, generally with fine wires.

The present experiments, made at the National Physical Laboratory during the early part of last year, have been interrupted and are still incomplete, but nevertheless we have been led to believe that, though there is much involved in the work which is obscure and demands further investigation, enough facts have been elicited to warrant the publication of a preliminary paper. More especially does this seem desirable as considerable attention is now being given to the nature and properties of the emissions from hot bodies.†

Thermal Sputtering.

The volatility of metals at temperatures well below their melting points is a familiar phenomenon to most workers. A homely example is provided by the blackening which is a common enough feature of carbon filament lamps and is occasionally displayed by tungsten lamps, especially when over-run. Sputtered images of a definite outline depending on the shape of the filament can sometimes be traced on the bulbs of carbon lamps.

The abnormal volatility of iridium has long been known to high temperature workers, in connection with its employment in thermocouples, furnace tubes and gas thermometer bulbs; the extent of the effect is sufficient to prohibit the use of iridium or its alloys at temperatures much above 1000° C.

Platinum is also known to exhibit a similar though much less marked

* Crookes, 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 461.

† A detailed account and discussion of the phenomena of ionisation by incandescent solid bodies is given in Chapter IX of Sir J. J. Thomson's 'Conduction of Electricity through Gases,' second ed., 1906. A more recent summary in considerable detail may be found in H. A. Wilson's 'The Electrical Properties of Flames and Incandescent Solids,' 1912. It has therefore not been deemed necessary to give here any account of the early work or a bibliography of the subject.

volatility; examples of sublimed platinum crystals are often found on the tubes of platinum-wound furnaces which have been subjected to prolonged use at temperatures up to 1400° or so.

The thermal disintegration of the platinum metals was first investigated gravimetrically by a group of workers—Berliner, Elster and Geitel, and Stewart in 1887–9. Holborn, Henning, and Austin,* took up the matter at the Reichsanstalt in 1903, from the point of view of the high temperature worker. In Sir William Crookes' experiments (*loc. cit.*), samples of the platinum metals were heated in still air at atmospheric pressure. His results indicate a decreasing volatility in the order Ru, Ir, Pd, Pt, and Rh; the effects were unexpectedly large.

The volatilisation of a metal increases rapidly with the temperature. In the case of platinum, iridium, and rhodium, the disintegration lessens as the pressure of the surrounding gas is reduced, and the effect would not therefore seem in these instances to be one of true sublimation. Roberts† has recently brought forward evidence that with these metals the volatilisation is effected through the intermediary of endothermic oxides more volatile than the metals themselves. It may be added that almost all workers are agreed that the presence of oxygen is essential to bring about the disintegration of most metals. Hydrogen and nitrogen are in general unfavourable to the effect.

Experimental.

After one or two preliminary trials, the apparatus described below was constructed and used in practically all the experiments. It is shown in fig. 1. Through a round iron plate, forming the support of a large glass bell-jar, were fitted near the circumference two insulated vertical brass electrodes (D, E) capable of carrying for short periods some hundreds of ampères without undue heating. Projecting inwards some 15 cm. from each electrode toward the centre of the jar was a stout iron strip (A, B) with its inner end bent upwards. To these iron strips were clamped adjustable jaws of the same material. The strip of metal (S) to be heated was gripped between these jaws in a horizontal position, edge upwards.‡ The strips employed were of uniform thickness and width but varied somewhat from sample to sample. The currents employed to heat them varied from about 50 to 250 ampères and the voltage across the strip from 0·5 to a maximum (rarely

* 'Phil. Mag.,' 1904, vol. 7, p. 388.

† 'Phil. Mag.,' February, 1913, vol. 25, p. 270.

‡ When necessary to prevent contamination of the metal of the strip where it touched the jaws, which sometimes became considerably heated, a platinum lining was fitted to the part where the metals were in contact.

reached) of about 5 volts. Most of the strips were approximately 5 mm. wide and 5 cm. long between the clamps; the emitting area was about 4 sq. cm. Larger specimens were used later in the study of iron and some other of the base metals.

Surrounding the strip and insulated completely from it was a metal cylinder (C) provided with one or two holes (H) for viewing the strip by means of an optical pyrometer. The cylinder was carried on an arm with suitable adjustments from an insulated support (F) passing through the base-plate of the apparatus. One pole of the strip was connected through a current-measurer to the cylinder, the whole of the circuit being everywhere carefully insulated from earth.

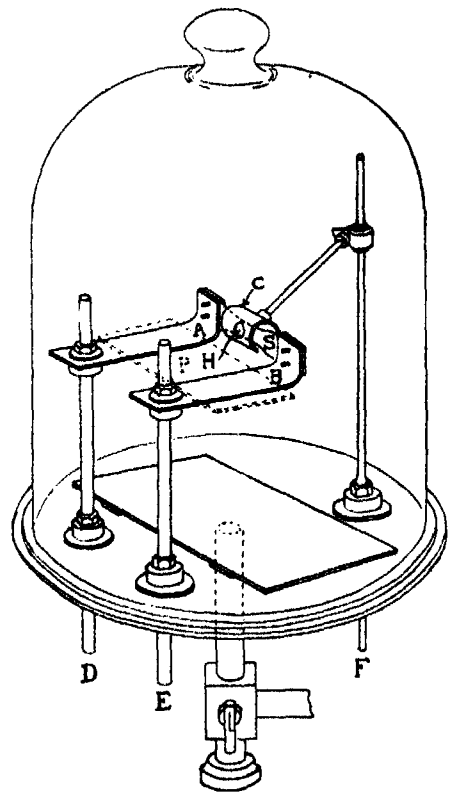

Fig. 1.

Heat Supply.

In order to avoid any local effects due to a different polarity at different parts of the strip, alternating current was always used for heating purposes. This was taken from a step-down transformer giving a number of variable ratios and voltages from 0 upwards. The primary current to the transformer was supplied from a motor-alternator, usually at a frequency of about 90 cycles. The field windings of the alternator were excited from a direct-current 100-volt supply. In series with the usual field regulator on the switchboard was arranged a convenient portable rheostat having a large number of segments. This could be manipulated by the observer at the optical pyrometer, who regulated the temperature of the strip as required. The control of the temperature was thus rendered extremely easy and accurate, and it was possible to maintain a strip at any given temperature to within a few degrees or even on the verge of melting for a considerable period.

In the later experiments the heating current and volts, and hence

approximately the energy expended in the hot strip, were measured by suitable alternating instruments.

Measurement of the Ionic Currents Produced.

The ionic currents generated varied from a fraction of a microampère to about 1/10 ampère. For the lower ranges a low-resistance moving-coil Sullivan galvanometer was used,* and for the higher values an arrangement was employed designed some time ago by one of us, primarily for study of the rapid changes in electrolytic conductivity of second class conductors. By means of this instrument, continuous and accurate current and volt measurements could be taken on the same galvanometer. Owing to the many different ranges of sensitivity, a large angular deflection was always available, if required, at any value of the current or voltage to be measured. On account of the very rapid changes in the currents obtained in most cases with rising temperature, some device of this kind was essential to convenient work.

Gases Employed.

In practically the whole of the experiments now to be detailed the gas employed was nitrogen of the ordinary commercial quality supplied by the British Oxygen Company and made from liquid air by the Linde process. The usual procedure, after mounting the strip in position, was to exhaust, by means of a rotary oil-pump, the large bell-jar, which served to cover the whole apparatus, and rinse out twice with nitrogen direct from the cylinder before the final filling and pressure adjustment. No special precautions were taken to secure either dryness of the gas used or great constancy of pressure during a run. Owing to the energy dissipated in the strip, amounting in some cases to a kilowatt or more, the upper parts of the apparatus usually became quite warm after five or ten minutes' run, and the pressures given are therefore only to be considered as approximate mean values. Pressures below a few millimetres of mercury were intentionally not employed, as it was desired to avoid pressures so low that the negative ion became the unencumbered negative electron. The experiments were conducted in nitrogen with the idea of using a gas which would be chemically inert to most of the metals.

* We were aware from the outset that it was more than probable, from the experiments of Strutt and other workers, that the same kind of effects as we were seeking could be obtained at relatively low temperatures if more delicate means of detecting minute currents had been adopted. We resolved, however, to study only the phenomena from the point of view of the currents generated being of ammeter rather than electrometer order, and therefore more sensitive current measurers were intentionally not adopted.

Measurement of Temperature.

The temperatures were measured by an optical pyrometer of the Holborn-Kurlbaum type made by Messrs. Siemens Bros. This instrument consists of a telescope of rather short focal length, in the focal plane of which is fixed the filament of a small incandescent lamp. In series with the lamp are a four-volt accumulator, a regulating resistance and an accurate ammeter. In taking an observation, the central portion of the horseshoe-shaped filament is matched in brightness with the object whose temperature is to be measured and the current through the lamp noted. Previous calibration of the arrangement serves as the basis of a table showing the connection between the current through the lamp and the temperature of the radiating object, applying, if necessary, the appropriate correction for want of "blackness" in the surface of the radiator. The observations are taken through an eyepiece consisting of one or more red glasses.

The absorbing device supplied with the instrument, consisting of two black glass mirrors, was used before the object glass in all cases, excepting a few of the observations at the lowest temperatures. In this arrangement the beam of light from the hot body is reflected twice at an angle of 45° incidence and thereby weakened to about 1/200th of its original intensity, thus allowing continuous observations to be made up to about 2700° C. without risk of over-running the pyrometer lamp. Observations even to the highest temperatures are easy and a practised observer can follow continuously the temperature of the strip to within a few degrees up to its melting point. Experience showed that, except the last two or three millimetres at each end, the temperature of the strips was generally very uniform. The temperatures recorded are, of course, black-body temperatures and are to some extent a function of the predominant wave-length in the red glass used in the pyrometer. In some of the curves below these black-body temperatures are reduced to true temperatures. As a rule, the error (of the order of 20° or so at 1500°) due to absorption in the glass walls of the bell-jar was unimportant.

Metals Employed.

We happened to have by us a number of suitable specimens of the platinum metals in the form of strip. On account of their relative chemical inertness, high melting-point and, as Crookes showed, their large volatility, we decided to use these for the earlier work. In the present experiments, platinum and iridium were employed; and, later on, the metals iron, tantalum, copper, nickel, and brass. The behaviour of the different metals is dealt with below.

Platinum.—The platinum strip when heated showed small positive currents

at about 1100°: at higher temperatures these became negative. Fig. 2 shows the relation between temperature and negative ionisation obtained in one experiment; the pressure was about 40 mm., the gas, nitrogen. The ionisation current increased rapidly as the pressure was lowered. Fig. 3 provides an example of this; the temperature of the platinum was maintained at about

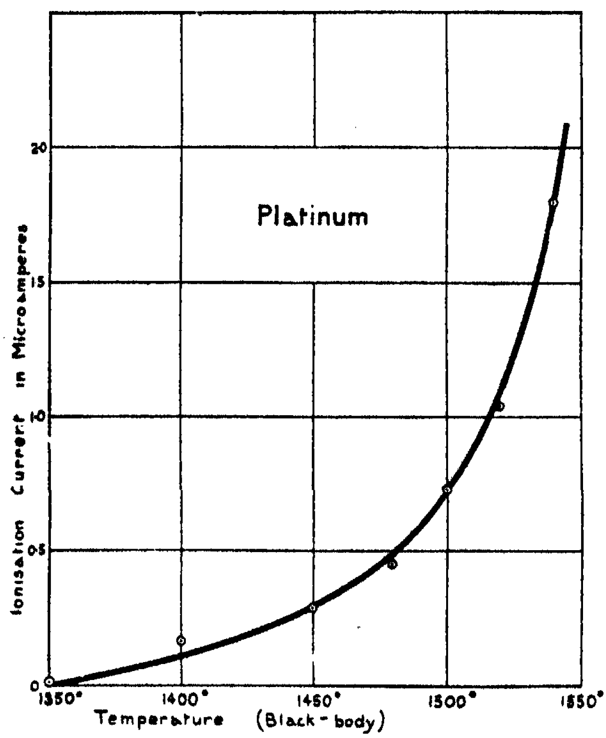

Fig. 2.—Platinum in Nitrogen at 40 mm. Pressure. Relation between Negative Ionisation and Temperature.

1460° B.B.: there was practically no sputtering either on the bell-jar or elsewhere.

Iridium.—At atmospheric pressure the iridium strip, when heated to high temperatures, emitted a black cloud of smoke, which ceased to be noticeable as the pressure was lowered. The volatility of iridium under such conditions is of course well known.

In one experiment with nitrogen at 4 mm. pressure the iridium gave a maximum positive current—about 2×10^{-7} ampère—at 1200° C., which, on cooling and reheating, did not attain more than a quarter of this amount.

At 1300° the negative current was plainly evident: it increased to 20 microampères at 1550°, and steadily rose until when the strip burnt out

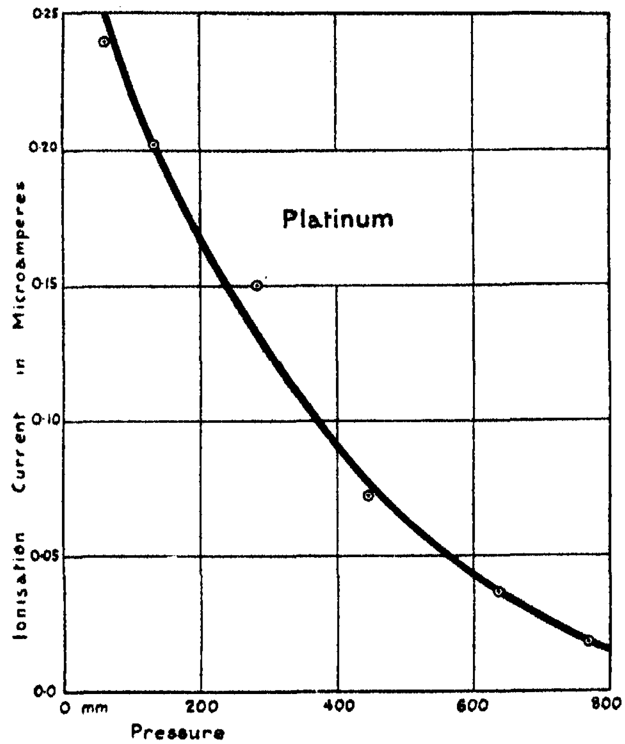

FIG. 3.—Platinum in Nitrogen. Relation between Negative Ionisation and Pressure.

(about 2300° C.) the current had attained 80 milliampères. Fig. 4 shows the growth of the current with temperature in this run. The higher temperature readings are somewhat doubtful owing to the increasing deposit on the bell-jar.

Iron.—Transformer iron was used in most of the experiments. The heating currents ranged from 40 to 150 ampères at voltages up to 2 or 3. No measurable ionisation current was detected at temperatures below 1100° in nitrogen at atmospheric pressure. At lower pressures a small positive current showed itself in some cases at about 1150° to 1250°. Occasionally for some reason the positive effect would persist right up to the melting point. Fig. 5 shows the relation between current and temperature at a pressure of 9 mm. The sputtering of the iron during this particular run was very great. As will be seen, the negative current increases very rapidly in the neighbourhood of the melting point. Fig. 6 shows a similar run at a rather higher pressure and somewhat lower temperatures.

Our experience certainly seemed to be that the greater the volatilisation, the greater were the currents recorded. In those experiments in which for

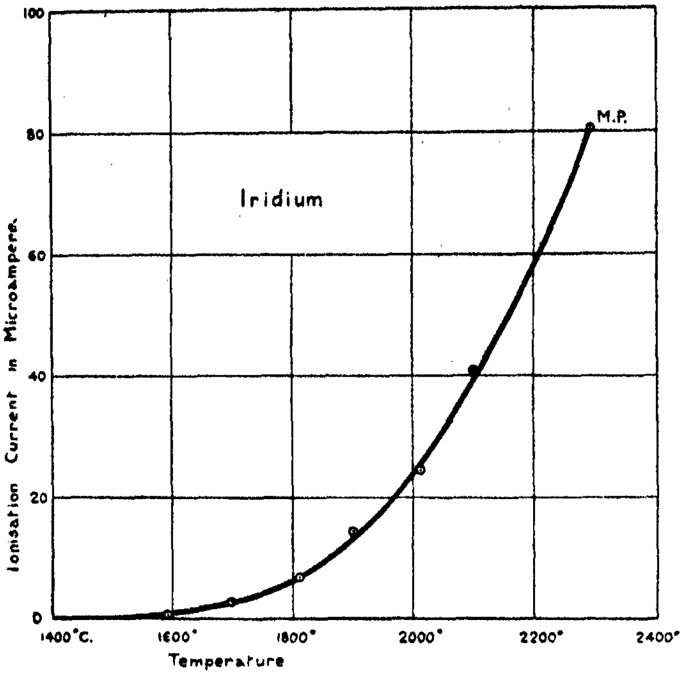

FIG. 4.—Iridium in Nitrogen at 4 mm. Pressure. Relation between Negative Ionisation and Temperature.

some reason the negative current was feeble or the positive current persistent, there was either feeble sputtering or none at all, *e.g.* in a number of experiments in which no sputtering was found, the currents at the melting point were 3 (−), 7 (−), 0·3 (+), 2 (−), 1 (+), 4 (−) microampères; while in experiments in which sputtering occurred the corresponding values were 88 (−), 60 (−), 66 (−) microampères.

The volatilised material when tested gave a strong iron reaction. We are unable to say at present what is the exact essential condition for successful sputtering, but we incline to the view that it is connected with the presence of traces of oxygen.

Tantalum.—The gas was nitrogen and the pressure 1 mm. As the temperature was run up a curl of smoke rose from the strip much the same as with iridium. We understand tantalum combines directly with nitrogen at high temperatures. At about 1000° a feeble positive current was evident; this changed to negative at about 1200°. At 1670° B.B. the negative current had increased to about 220 microampères. Fig. 7 shows the variation of the ionisation current with temperature.

The tantalum on this occasion yielded a very considerable deposit, which when analysed proved to be nearly all tantalum with a trace of iron.

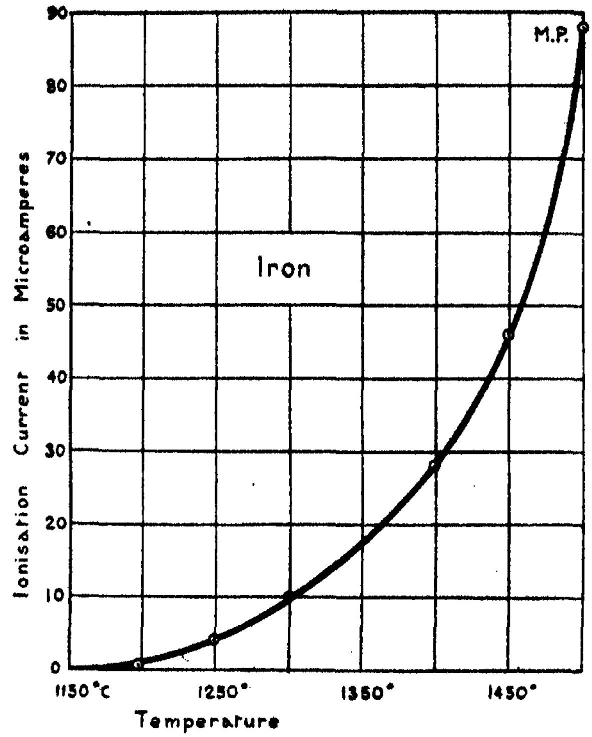

FIG. 5.—Iron in Nitrogen at 9 mm. Pressure. Relation between Negative Ionisation and Temperature. Large Sputtering.

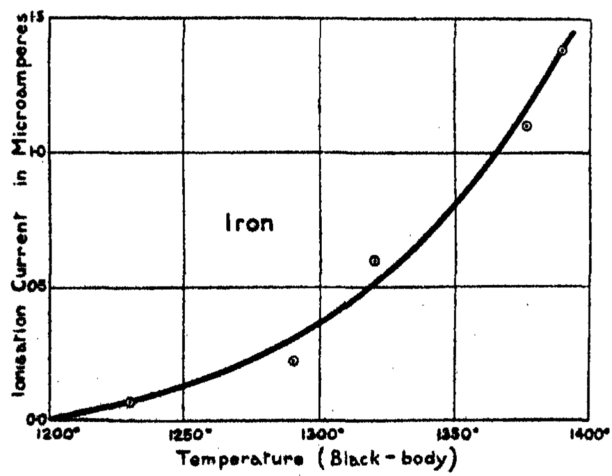

FIG. 6.—Iron in Nitrogen at 12 mm. Pressure. Relation between Negative Ionisation and Temperature. Slight Sputtering.

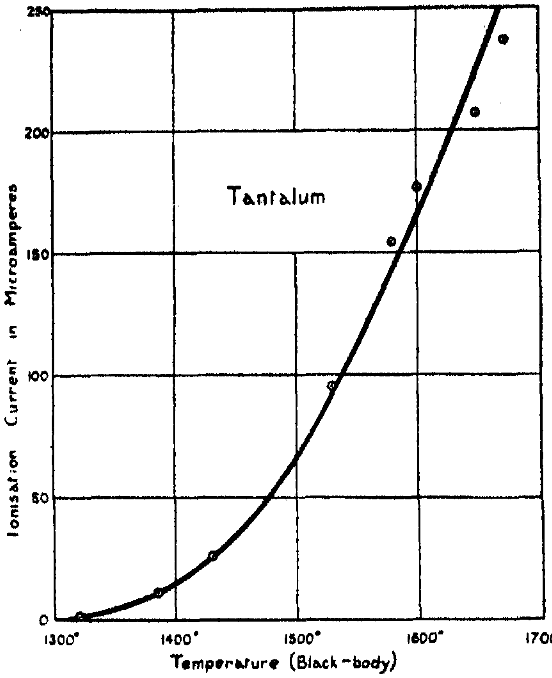

FIG. 7.—Tantalum in Nitrogen at 1 mm. Pressure. Relation between Negative Ionisation and Temperature.

On a second heating at a slightly higher pressure there was very little sputtering, and the highest current recorded at about 1660° B.B. was about 50 microampères. Heating currents up to 80 ampères and 4·6 volts were employed.

Nickel.—Nitrogen at 4 mm. pressure. Heating current up to 80 ampères. There was no sputtering. Small positive currents were recorded from 1200° upwards; they increased suddenly to about 1 microampère as the strip melted (1440° C.).

Copper.—Nitrogen at 4 mm. pressure. Heating current up to 200 ampères. Small positive currents from 1000° upwards; a larger positive current flashed on the galvanometer as the copper melted (1080° C.). At higher pressures, this final current was smaller, *e.g.* 5×10^{-8} at 55 mm. Hg.

Brass.—Nitrogen at 3 mm. pressure. Heating current up to 110 ampères and 1·8 volts. There was no noticeable sputtering. At temperatures of 900° upwards small positive currents were noticed, which at the instant when the brass melted (about 1000°) became momentarily much larger. The fused ends of the strip showed very plainly the copper present.

Carbon.—From our experience with carbon at atmospheric pressure we

anticipated that the sputtering would be greatly enhanced by a reduction of pressure. On trying the experiment with a carbon rod of unusually high purity, in a good vacuum, we were surprised with the result, for only a very slight deposit was obtained, and this was whitish and obviously due to traces of silica, etc., present in the carbon. The copper cylinder was absent and the temperature employed was about 2000° C.

A similar negative result was obtained from an experiment conducted with Acheson graphite in a hydrogen vacuum, and a temperature probably exceeding 2500° C. Incidentally, evidence was obtained in these experiments of the softening of carbon at temperatures from about 2500° upwards. Two special clamps were made, and as they were not quite in alignment the carbon rod was clamped under lateral strain. At the end of the run it was found that the rod, originally straight, was now crooked; the carbon had evidently been plastic enough to accommodate itself to the strain. The result is interesting having regard to a recent controversy on the subject. Fig. 8 shows the carbon rod before and after the experiment.

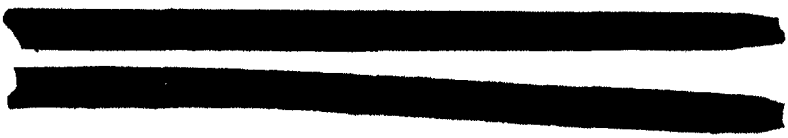

FIG. 8.

We were tempted to return for the moment to an experiment at atmospheric pressure. AB (fig. 9) is a rod of specially pure carbon

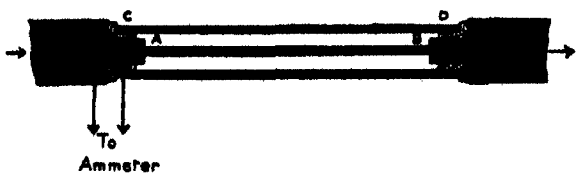

FIG. 9.

containing only about 0·1 per cent. of impurity (chiefly silica). The ends were mounted in graphite blocks, and the rod was surrounded by a carbon cylinder (CD) insulated with bushes of mabor brick. The cylinder served as the "cold" electrode, and was joined through an ammeter to the inner rod, which was heated by transformer current and made as hot as our resources would permit (probably not far from 3000° C.). The current used was of the order of 1000 ampères, the energy about 10 kilowatts. The outer cylinder rose to about 1100° C., and under these conditions the ammeter recorded a steady ionisation current of about 3½ ampères. The degree of

ionisation of the gas between the electrodes is, of course, phenomenal, and its conductivity akin to that of a metal.

A repetition of an earlier experiment mentioned in our previous paper took the form of a carbon tube, down the centre of which was passed a metal tube cooled from within by a rapid stream of water. The carbon tube was heated by low-voltage alternating current to about 2500° C., and hydrogen was passed between the two tubes. Most of the impurities in the carbon had been removed by continued heating previously; and on withdrawing the metal tube at the end of half an hour or so it was found to be coated with a deposit of carbon, hard enough and coherent enough to be slid off in short lengths. Fig. 10 shows two examples of such carbon. The method is of

FIG. 10.

interest as furnishing a possible means of obtaining by fractional distillation carbon of a purity unattainable by other methods. During this experiment ionisation currents up to about 1 ampère were recorded.

It certainly seems that the large ionisation effects obtained with carbon at higher pressures are due to the chemical activity of the carbon, for which the presence of gas in quantity is essential.

Positive Currents.

The emission of positive electricity was found to occur between about 900° and 1400° C. In the case of metals which melt within this range a sudden and striking increase in the positive current at the melting point was sometimes remarked with samples which had not been heated for more than a few minutes. There were two factors which helped to display this effect to advantage; one, the nicety of control over the heating, by which it was possible to hold the temperature just below or on the melting point for some time; the other, the large size of the samples which served both to enhance the effect and to give the metal some ability to hold together at the melting point. In some instances the slow local fusing of part of the strip was watched in the pyrometer while temperature measurements were being taken.

The positive currents obtained from most bodies at moderate temperatures are now pretty generally attributed—at any rate in part—to the escape of occluded gas, which leaves the metal in an ionised condition. The escape of this gas would naturally be greatly facilitated when liquefaction of the

metal occurred, and it is to this cause we think the momentary increase in the positive current at the liquefying point is due. *En passant*, we may note that our general experience with most of the metals we have tried has been that the positive current is augmented by the presence of oxygen.

The positive current readings were not steady or reproducible under specified conditions—the currents usually drop considerably after a few minutes' heating, and this without altering the temperature or pressure in any perceptible way.

Negative Currents.

As will have been remarked, the negative ionisation increases rapidly with the temperature: the various curves shown above, connecting temperature and current, are all exponential in character. It should be pointed out that in all cases the currents are unsaturated; no potential whatever is applied to the hot metal apart from the small variable potential due to the alternating heating current. The negative ions must accordingly derive their velocity directly or indirectly from the heat of the strip, or from some chemical reaction between the strip and the gas.

Sir J. J. Thomson* showed that charged particles of metal were among the carriers of current in the positive discharge from a hot platinum wire. We believe that they are also often present in the negative discharge obtained from metals at higher temperatures, and that while the negative current at moderate pressures is usually due mainly to the negative gas ion, the current is largely augmented if the conditions are such that particles of metal also cross between the two electrodes. These conditions are probably secured by the presence of a gas to which the metal is chemically responsive —with most metals oxygen is so effective. Thus the ionisation current is to be regarded as a direct manifestation of the chemical energy of combination. With this view in mind we tried to exaggerate the effect by burning iron and magnesium wire in oxygen, the wire being surrounded by an outer cylinder, with a galvanometer in circuit between the wire and the cylinder. We tried various forms of apparatus, but the experiments were interrupted before we were completely assured of their success.

If it should be that, at any rate at higher pressures, the ionisation current from hot metals is in some instances carried chiefly by particles of the metal, we have the means of deriving a mean value for the ratio of the charge to the mass (e/m) for the particles. For example, in one experiment with iridium, conducted in nitrogen at a pressure of about 20 mm. and a temperature of 1360° B.B., the iridium strip lost 1·1 mgrm. in 11 minutes; of this

* J. J. Thomson, 'Conduction of Electricity through Gases,' 1906, second ed., p. 217.

0·9 mgrm. was received by the cylinder. The mean ionisation current during this time was 0·56 microampère. Whence $e/m = 0{\cdot}4$ E.M.U. grm.^{-1}, and assuming that each particle carries unit charge,

$$m = 3{\cdot}8 \times 10^{-19} \text{ grm.}$$

Now the mass of the iridium atom is about $3{\cdot}2 \times 10^{-22}$ grm., so that the average number of iridium atoms in one particle is 1200.

Apropos of the source of the ionisation current, it may be added we have repeatedly noticed that if the metal is hot enough to be giving out negative electricity, and is allowed to come into actual contact with the surrounding colder cylinder, the galvanometer shows a large current in the reverse direction. The thermal E.M.F. is thus opposed to the ionisation potential. This remark holds equally well for a hot carbon rod in an outer cylinder of cold carbon.

Straight Line Projection of Particles.

While there is no doubt that a good deal of the deposit which we obtained in these experiments was due to volatilisation and condensation as ordinarily understood, we think that this is not the whole explanation, and that the effect is partly due to the straight line emission of particles of matter from the heated metal.* Under most conditions, it is true, this rectilinear propagation is confused by general sublimation, but we have noticed it on several occasions when the circumstances were favourable. In one experiment a strip of iridium (S) was heated, edge upwards, in nitrogen at about 20 mm. pressure. At the end of the run it was noticed that there were two horizontal bands of deposit (A and B, fig. 11) on the inside of the copper enclosing cylinder, each one opposite and roughly the same width as the vertical face of the strip. At points C and D opposite the edge of the strip there was little or no deposit.

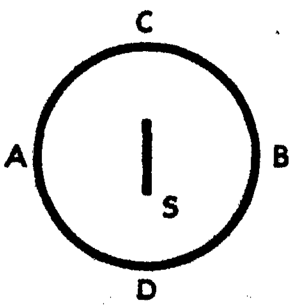

Fig. 11.

Fig. 12 is a photograph of the iron deposits obtained on the bell-jar, in the proximity of the brass uprights D, E (fig. 1). In this experiment there were two holes (H) side by side in the cylinder C. The photograph is possibly to be regarded as showing much distorted projections of the uprights D and E, by particles of metal shot from the heated strip, through the holes in the cylinder.

But this is probably not a complete explanation of the photograph. The pressure during this run was about 2 mm., not too low to prevent convection

* See, in this connection, Reboul and de Bollemont, 'Journ. de Phys.,' July, 1912.

currents controlling the sublimed iron vapour, which, as the deposit all over the bell-jar shows, was everywhere present. In this experiment, the iron

FIG. 12.—Iron Deposit.

strip was heated for some minutes and the brass uprights D, E, and iron strips A, B, got appreciably warm—warm enough doubtless to cause an upward current of gas to oppose the descending iron vapour, and to cause it to deposit on the glass adjoining. The successive bands of deposit at each of the crests are certainly interesting and suggestive of a kind of spectrum which might be produced by a magnetic or electric field acting on charged particles of metal with velocities grouped around certain values. But the only possible source of such a field is the alternating heating current, and even taking the maximum values of the current and potential the strength of the magnetic or electric field which could be produced is entirely inadequate to deflect and disperse charged particles whose masses are as large as we believe them to be.

FIG. 13.—Iridium Deposit.

We are not in a position to explain the various peculiarities the photograph displays; fig. 13 is a corresponding photograph in the case of iridium.

Summary.

Preliminary experiments have been carried out on the volatilisation and electrical emissivity of a number of metals, mostly in nitrogen at reduced pressures. The metals were heated by alternating current and no applied potential was employed.

(1) The emission of positive electricity occurs at temperatures from about 1000° to 1400° C. For metals which melt within this range, a sudden and marked increase in the positive current often occurred at the liquefying point—due probably to the sudden release of occluded gas.

(2) Oxygen appears to augment the positive current.

(3) At higher temperatures, negative electricity predominates and increases rapidly with the temperature. The negative current attained with iridium at the melting point was 80 milliampères, with tantalum at 1670° C. 220 microampères, with iron at the melting point 90 microampères. In the case of carbon in air at atmospheric pressure, an ionisation current of $3\frac{1}{2}$ ampères was obtained.

(4) The negative current at moderate pressures appears to be largely increased if the conditions are such that considerable sputtering of the metal occurs.

(5) The negative currents are probably a consequence of chemical reaction between the metal and the surrounding gas.

(6) Carbon becomes plastic in the neighbourhood of 2500° C. At such temperatures it also readily sublimes.

We should like to thank Mr. H. C. Booth, of the National Physical Laboratory, for his sketch of the apparatus (fig. 1).

An Active Modification of Nitrogen, Produced by the Electric Discharge.—V.*

By the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received May 9,—Read June 19, 1913.)

§ 1. *Improved Technique.*

Experience has led to certain modifications of detail in preparing nitrogen for the experiments. Commercial nitrogen from cylinders is still used, but instead of passing it over phosphorus it is allowed to stand in contact with it for some hours. The former method does well enough when the phosphorus is freshly cut, but in time the surface deteriorates, owing, in part at least, to the accumulation of oxides of phosphorus, which tend to obstruct access of the gas.

Two 15-litre aspirator bottles are arranged as a gasholder in the usual way, the gas being displaced by water. In the gas space is hung up a muslin bag containing chopped phosphorus. On filling the gasholder with commercial nitrogen the phosphorus fumes freely, and all traces of oxygen are removed in the course of two or three hours. The fumes subside, and the gas is ready for use. It merely requires drying on its way to the discharge tube. This 15-litre supply is more than enough for most experiments. When it is used up the water rises and drowns the bag of phosphorus, dissolving out the oxides which have been formed, and leaving it in good condition for use next time.

It is advisable to cover the gasholder with a jacket of black cloth to exclude light, which spoils the phosphorus surface. With this precaution such an apparatus will remain in good order for a year or more. Air should not be drawn into it. If this is done the phosphorus will probably catch fire.

It may be thought inconvenient to intermittently fill up the gasholder, instead of working straight from the supply in the cylinder. In practice this disadvantage is more than compensated. In using the gas it is convenient to be able to measure the rate of intake, which is readily done if the gasholder is graduated.†

* I, 'Roy. Soc. Proc.,' A, vol. 85, p. 219; II, *ibid.*, A, vol. 86, p. 56; III, *ibid.*, A, vol. 86, p. 262; IV, *ibid.*, A, vol. 87, p. 179.

† The bottle holding the displaced water is the most convenient one to graduate, as it does not need to be kept covered from the light.

Moreover, it is advantageous to dispense with the automatic gas regulators, which, as obtained commercially, give an inconveniently high gas pressure, and are apt to leak, so that more nitrogen is wasted than is used.

§2. *Effect of Impurities in the Nitrogen used.*

It has been thought by some of those who have repeated my experiments* that the phenomena of active nitrogen are not obtained in the absence of traces of oxygen. Others† have confirmed the original conclusion that nitrogen alone is concerned. For my own part I am more than ever confident of the correctness of this view. Since the question has been raised I shall enter into my reasons more fully than would otherwise have been thought necessary.

As explained (§1) the nitrogen used habitually in the experiments has stood over phosphorus until all action is over and all fume has subsided. Moreover, the issuing nitrogen is saturated with phosphorus vapour, as is shown by letting it blow off into the air in a dark room, when the issuing jet of gas becomes luminous by mixing with atmospheric oxygen. The question then arises, how much oxygen at the most can be present in such nitrogen?

To settle this a flask of 1500 c.c. capacity was filled with commercial nitrogen, and allowed to stand over water in a pneumatic trough. A piece of phosphorus was supported in the middle of the flask, and in the course of a few hours removed most, at any rate, of the residual oxygen. The gas volume was then quite free from fume, and in the dark no luminosity whatever could be seen in it. A bubble of air, 1/20 c.c. in volume, was then passed up into the flask,‡ which was enough to produce distinctly visible streaks of white fume. These were distributed throughout the greater part of the volume, showing that the oxygen introduced was no longer locally concentrated. With 1/10 c.c. of air the streaks were most conspicuous, and could not escape even careless observation. From this experiment it appears that the addition of a 1/150000 part of oxygen produces a distinct reaction. It seems pretty safe therefore to conclude that not more than 1/100000 part of oxygen can remain when the phosphorus has done its work. Probably even this fraction would be an enormous overestimate of the actual amount.

* See F. Comte, 'Phys. Zeit.,' 1913, vol. 14, p. 74; also E. Tiede, 'Ber. d. Deutsch. Chem. Gesell.,' 1913, p. 340.

† König and Elöd, 'Phys. Zeit.,' 1913, vol. 14, p. 165.

‡ It is scarcely necessary to describe the simple arrangement used to measure out and deliver this small quantity of air.

Thus the phosphorus purification seems to secure the complete absence of oxygen. In addition the gas has been passed on occasion through a tube 80 cm. in length, tightly packed with rolls of fine copper gauze, and heated to full redness. The gauze had been oxidised and reduced beforehand to make its surface spongy. I do not find that the copper makes any difference whatever to the phenomena. Naturally therefore it has been discarded.

This result with copper is in direct contradiction with one of my critics (Comte). How to account for his result I do not know. The whole weight of the decision as to whether oxygen is necessary must rest on direct experiment. But I would ask those who may not have an opportunity of seeing or repeating the experiments to give a little consideration to the *a priori* probabilities. The active gas is capable of forming nitrides from the metals, and hydrocyanic acid from hydrocarbons. What possible *rôle* is there for oxygen, admittedly in infinitesimal proportions only, in such a process?

We may next consider the effect of intentionally adding oxygen to the nitrogen used, starting with nitrogen which had been purified by phosphorus. The unfavourable effect of oxygen has already been considered.* It was now systematically investigated, mixtures of known composition being made up and passed through the discharge tube. One per cent. of oxygen (by volume) was found to very materially diminish the volume and brilliancy of the active nitrogen glow; 2 per cent. obliterated it altogether. With 5 per cent. of oxygen a totally different phenomenon, the ozone-nitric oxide glow,† begins to come in. These experiments indicate that to get good results the nitrogen should certainly not contain more than 1/10 per cent. of oxygen. As already shown, nitrogen purified in the cold by phosphorus more than fulfils this condition.

The effect of other impurities likely to be present was also studied.

The addition of 20 per cent. of hydrogen extinguishes all glow; $\frac{1}{2}$ per cent. of hydrogen, on the other hand, scarcely does any harm. It is seen that traces of hydrogen produce far less effect than traces of oxygen. Practically if the H_α line cannot be distinctly seen in the exciting discharge, outshining the nitrogen bands in the same region of the spectrum, it may be concluded that no prejudicial quantity of hydrogen is present.

Carbon dioxide hinders the glow about as much (or as little) as hydrogen. The presence of water vapour is much more prejudicial. Scarcely any glow is obtained from nitrogen drawn straight from the gasholder without drying, and therefore saturated with water vapour.‡

* I, p. 224; II, p. 56.

† 'Phys. Soc. Proc.,' December 15, 1910.

‡ It is of course no longer saturated after it has passed the regulating stopcock, and is many times expanded.

To get the best results very good drying is required. Two alternative drying tubes were arranged in parallel. A two-way stopcock made it easy to exchange one for the other. Each contained well packed phosphorus pentoxide; one column of this material measured about 6 cm. × 2 cm., the other about 30 cm. × 5 cm. The glow was markedly better developed with the second. Even when this had done its work a further slight improvement was obtained by passing the gas through a tube cooled to liquid air temperature, and packed with copper gauze, to provide a large condensing surface. It has not been determined whether the advantage of this last purification is in further drying, or in removal of traces of hydrocarbons and phosphorus vapour. The latter certainly is removed.

§ 3. *Chemical Action on Elements—Metallic and Non-Metallic.*

In the earlier work* the proofs of chemical union with active nitrogen chiefly relied upon were increase of weight in the substance acted upon, and disappearance of the gaseous nitrogen used. I have now gone over most of the ground by the alternative method of testing for ammonia when the products are boiled with water or caustic potash solution. This method has proved much easier and more powerful than the previous ones.

Mercury, it will be remembered,† gave an explosive compound when its vapour was allowed to mix with active nitrogen. Shaking the product with water, and filtering, a strong reaction of ammonia is obtained with Nessler's solution.‡ It was observed, too, that specimens of the compound which had lain exposed to the air for some days no longer gave the characteristic crackling explosions on heating. Presumably the nitride had been decomposed by atmospheric moisture.

Zinc and cadmium distilled below a red heat in a current of active nitrogen also yield nitride, which is not explosive, however. Boiled with water the contents of the tube give a strong Nessler reaction in each case. Blank experiments, in which the conditions are in all respects the same, except that the stream of nitrogen is not made active, gave absolutely negative results.

With all these metals the product forms an adherent black coating on the walls of the tube, and apparently retains mechanically an excess of the metal condensed from its vapour.

* I, pp. 222–225.

† I, p. 225.

‡ In this and the following experiments, the indication obtained was not merely a discoloration, but an abundant red precipitate making a quantity of liquid quite opaque.

Sodium vaporised in the nitrogen stream also gave a nitride, decomposable by water, and detected as before. This action appears to be somewhat less energetic than those just mentioned. But the first part of the distillate from the alkaline solution gave a strong Nessler reaction. It was thoroughly verified that sodium from the same stock, not treated with active nitrogen, gave no such reaction.

Arsenic sublimed in active nitrogen and boiled with potash solution gave ammonia, readily detected in the distillate. Sulphur did the same. Occasionally traces of the blue compound obtained so abundantly with carbon disulphide (see below) appeared in this instance. More commonly the product was not visibly distinguishable from the excess of sulphur. It probably consists of the ordinary yellow sulphide of nitrogen.

A quantity of iodine was allowed to sublime at room temperature, in a stream of active nitrogen. The usual brilliant blue glow was produced.* The iodine, together with any product that might have been formed, was frozen out with liquid air and dissolved in potash. No trace of ammonia could be obtained from the solution.

§ 4. *Chemical Action on Inorganic Compounds.*

When carbon disulphide vapour is fed into a stream of active nitrogen, it is soon noticed that a solid deposit forms on the walls of the vessel. This deposit forms evenly over a considerable area, and has a deep indigo blue colour. In the experimental arrangement the gas stream was laid on through a tube cooled in liquid air to remove excess of carbon disulphide. Here it was observed that a further deposit of brown colour was formed on the cooled surface.

First, as regards the blue deposit. This oxidised with strong nitric acid yields sulphuric acid, identified by its action on barium chloride solution. Sulphur, then, is one constituent element.

Heated with potash solution the blue substance dissolves† and ammonia is liberated, indicating the presence of nitrogen.

The blue substance is identified with the blue sulphide of nitrogen obtained by Burt,‡ to which he assigned the composition $(NS)_x$. Like his preparation, it proved insoluble in benzene and in chloroform.

The brown deposit separated on the cooled condenser remains to be considered. It was soluble in hot concentrated sulphuric acid to a

* I, p. 227 ; see also coloured plate, p. 228.

† A thin colourless skin is left on the glass, which has not been investigated further.

‡ 'Trans. Chem. Soc.,' 1910, vol. 97, p. 1171.

brown-purple solution, and in concentrated nitric acid to a red solution. This behaviour, taken in conjunction with its formation from carbon disulphide, identifies it as the polymeric carbon monosulphide obtained by Dewar and Jones* by the action of the silent discharge on carbon disulphide vapour. Apart then from the unknown molecular weight of the solid product, the action may be represented thus

$$CS_2 + N = NS + CS.$$

Vapour of chloride of sulphur, fed into active nitrogen, yields a light yellow deposit, which consists, at all events in part, of ordinary sulphide of nitrogen. Heated with potash, it yields ammonia in abundance.

Hydrogen sulphide behaves similarly. In each case the luminosity developed is blue and shows bands due to sulphur.

The magnificent luminous effects obtained with stannic chloride have already been mentioned.† The energy of the chemical action does not seem to be proportionate. A small quantity of white deposit forms on the tube walls, but it is difficult to collect enough for examination.

Titanium tetrachloride, which develops a brilliant titanium line spectrum on mixing with active nitrogen, gives a much more abundant white deposit. This yields ammonia when boiled with potash, but is not dissolved. It is soluble in acids and appears to be a compound of titanium, chlorine, and nitrogen. Its further study may be undertaken later.

§ 5. *Chemical Action on Vapours of Organic Substances.*

It was previously shown‡ that acetylene reacted with active nitrogen to yield a cyanogen compound. The proof was: (1) development of the cyanogen spectrum; (2) formation of a cyanide by absorption in alkali. Other organic compounds also develop the cyanogen spectrum, and it was assumed that they also form cyanogen.

The subject has now been examined more fully, though much still remains to be done. In order to condense out the products of reaction, the gases were passed through the vessel shown in fig. 1, with the result that they were frozen on the outside of the test-tube. This could be withdrawn after the experiment, and quickly inserted into another larger test-tube, by means of the same rubber cork (fig. 2). In the bottom of the outer tube was a little potash solution. As the products evaporated they were absorbed by agitation in this solution, which could then be examined.

* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 527; 1911, A, vol. 85, p. 574.

† I, p. 226; also Strutt and Fowler, 'Roy. Soc. Proc.,' 1911, A, vol. 86, p. 110.

‡ I, p. 228.

The advantage of this method is that the cooled test-tube is readily taken out and replaced for the next experiment without disturbing other parts of the apparatus. The following compounds were tested and gave the Prussian blue reaction strongly: acetylene, benzene, pentane, methyl bromide, ethyl

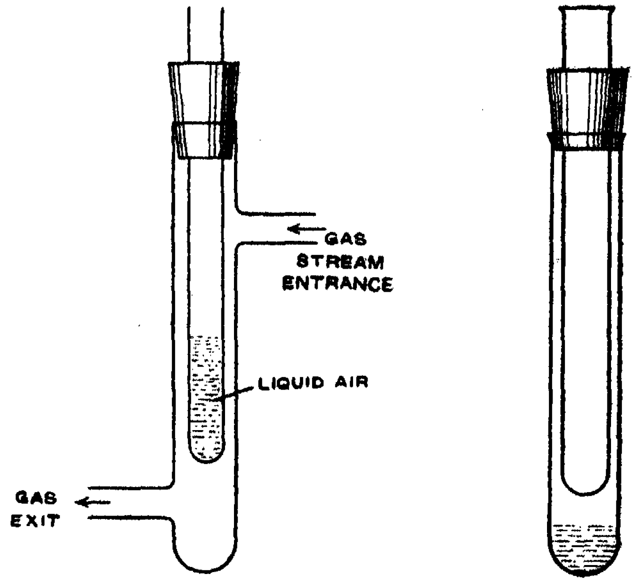

FIG. 1. FIG. 2.

chloride, ethyl iodide, chloroform, bromoform, ethylene dichloride, ethylidene dichloride, and ether. Carbon tetrachloride and carbon disulphide, in sharp contrast with the above, gave no trace of it.

No evidence was brought forward in previous papers to decide whether the compound formed in these cases is cyanogen gas or hydrocyanic acid.

The reactions of these substances with alkali are as follows:—

$$HCN + KOH = KCN + H_2O,$$
$$C_2N_2 + 2KOH = KCN + KCNO + H_2O.$$

We may therefore hope to decide between the two alternatives by looking for a cyanate in the liquid. The test for cyanate used was very kindly shown me by Dr. M. O. Forster, F.R.S. The liquid (as concentrated as possible) is just acidified with acetic acid, and a cobalt solution added. In the presence of cyanate a brilliant blue colour is produced.

This test was applied to the product from three hydrocarbons, pentane, acetylene, and benzene,* and gave absolutely negative results. It is

* In the two latter cases the solutions had to be decolorised with animal charcoal before the test could be applied.

concluded that the product from hydrocarbons is hydrocyanic acid, not cyanogen gas.

Compounds containing the halogens behave differently. With chloroform and carbon tetrachloride,* a strong cyanate reaction was obtained. It seems probable that in these cases cyanogen chloride is formed, which (as is known) yields cyanate when treated with alkali.

The evidence above presented is not enough to determine completely the course of the reaction when active nitrogen acts on these organic vapours. We need not hesitate, indeed, to represent it in the case of acetylene by the equation

$$C_2H_2 + 2N = 2HCN,$$

and similarly in the case of benzene.

This, however, is not a complete account of the matter. More complex solid or liquid products of dark colour are formed in addition. With benzene these have a characteristic odour. Dr. Forster, to whom they were submitted, felt fairly certain that cyanobenzene, C_6H_5CN, was present, and probably also the isomeric phenylcarbylamine C_6H_5NC. It seems not improbable that there is here the germ of a new method of organic synthesis, which I hope may be taken up by those competent to pursue it.

With pentane and similar bodies the question remains unanswered—what becomes of the surplus hydrogen, over and above that required for the formation of hydrocyanic acid? The probable alternatives are (1) it is set free, or (2) it unites with more of the active nitrogen to form ammonia. Neither possibility lends itself very easily to experimental test. Ammonia is indeed easily obtained from the products by the action of caustic alkali, but this proves nothing, for it may come wholly from the decomposition of hydrocyanic acid by the caustic alkali used.

Little or no dark-coloured matter is produced when active nitrogen acts on pentane vapour. Chloroform does yield a little, however, under some conditions.

It is of interest to inquire what fraction of the nitrogen passed through the apparatus is converted into hydrocyanic acid, when allowed to react with excess of some organic vapour. In a typical experiment light petroleum, mainly pentane, was used. Six litres of nitrogen were passed, the products frozen out, and afterwards absorbed in potash. The excess of petroleum floated as a layer on the alkaline solution, and was got rid of by burning it off. The cyanide was estimated by Liebig's volumetric method; 15·5 c.c. of decinormal silver solution sufficed to just give a permanent turbidity.

* The latter, it will be remembered, gives no cyanide.

This indicates about 37·4 c.c. of combined nitrogen, measured as nitrogen gas at room temperature, *i.e.* 0·62 per cent. of the nitrogen passed. This is about the same as the yield of combined nitrogen obtained in earlier experiments in the reaction with phosphorus,* but much less than in the reaction with nitric oxide.† I do not now look on any of these estimations as indicating the percentage of active nitrogen generated under the experimental conditions, though of course they are inferior limits to it. Probably much of the active nitrogen reverts to ordinary nitrogen without entering into chemical union with the reagent presented to it.

§ 6. *Luminosity Accompanying these Actions.*

It was remarked‡ that the various organic vapours differ very much in the intensity of the cyanogen spectrum which they yield when mixed with active nitrogen. In cases like benzene the spectrum is scarcely to be seen, and this was thought (*loc. cit.*) to indicate that very little hydrocyanic acid was formed.

The chemical tests have shown, however, that it is formed quite as abundantly from benzene, which scarcely gives the cyanogen glow, as from acetylene, which gives it magnificently.

Again, if ready-made cyanogen is fed into active nitrogen we get the cyanogen glow brilliantly, but anhydrous hydrocyanic acid vapour gives little or nothing of it in the same circumstances. These cases are of interest because in them we have to do with ready-made molecules, and are independent of any special phenomena which may occur at the moment of their formation.

Not only does the absolute intensity of the cyanogen glow differ very much from one compound to another, but also the relative prominence of the red series of bands.§ Further investigation has shown that a special development of the red bands is always associated with the presence of the halogens. Carbon tetrachloride, chloroform, bromoform, ethylene dichloride, and ethylidene chloride all gave a strong orange cyanogen glow. Ethyl chloride and methyl bromide gave one of intermediate character, while in all the cases examined, in which halogens were not present, the glow was lilac. I am inclined to associate the orange glow with cyanogen chloride or bromide. This view is strengthened by the observation that vapour of cyanogen chloride fed in directly yields it in great intensity.

* I, p. 223.

† II, p. 58.

‡ I, p. 228.

§ I, p. 228; also Strutt and Fowler, 'Roy. Soc. Proc.,' 1911, A, vol. 86, p. 113.

In spite of the large number of additional facts accumulated it is still difficult to decide definitely what connection exists between the luminous phenomena developed by active nitrogen, and its chemical actions. The following points may be noted: When the nitrogen stream acts on elementary bodies the spectrum of the element developed may be one of lines (mercury, sodium, the metals generally) or of bands (sulphur, iodine). In the former case chemical action appears always to be traceable. In the latter it is traceable in some cases (sulphur); in others not (iodine). When the action is on a compound the spectrum developed may be a band spectrum of the compound introduced (cupric chloride, tin tetrachloride, mercury haloids), a line spectrum of one of the elements contained in it (titanium tetrachloride), a band spectrum of one of the contained elements (hydrogen sulphide), or a band spectrum of a compound formed in the reaction (cyanogen spectrum from acetylene). Finally, an energetic action may be going on without any very distinct emission of light (benzene).

There is evidently no simple generalisation to be extracted from such facts as these, and it is best perhaps provisionally to regard the luminous effects as quite independent of the chemical ones. On this view, if a suitable substance, elementary or compound, happens to be present, it will draw energy in some way from the active nitrogen, and emit a characteristic spectrum; and this no matter whether the substance is introduced in the first instance as such, or results from chemical combination or decomposition.

§ 7. *Summary.*

(1) An improved practical method of preparing and storing nitrogen for the experiments is described.

(2) It is shown, notwithstanding criticisms of certain other experimenters, that the presence of traces of oxygen in the nitrogen used is not essential, or even favourable, to the phenomena. The nitrogen used, purified by cold phosphorus, does not contain oxygen to the extent of one part in 100,000. Passing it over red-hot copper in addition makes no difference. The intentional addition of oxygen does harm; 2 per cent. obliterates the effects altogether. Hydrogen and carbon dioxide as impurities are much less harmful, but traces even of water vapour have a very bad effect.

(3) Nitrides are formed by the admixture of active nitrogen with vapour of mercury, cadmium, zinc, arsenic, sodium, and sulphur. These are decomposable by water or potash solution, yielding ammonia.

(4) Carbon disulphide yields a blue polymeric nitrogen sulphide, and polymeric carbon monosulphide. Chloride of sulphur gives ordinary yellow

nitrogen sulphide. Stannic chloride and titanium tetrachloride also yield solid products. In the latter case nitrogen was proved to be present.

(5) All organic compounds tried, except carbon tetrachloride, yield hydrocyanic acid freely, but not cyanogen, as was proved by chemical tests. When chlorine is present, cyanogen chloride is formed. Benzene yields (almost certainly) cyanobenzene.

(6) The intensity of the cyanogen spectrum with organic compounds is no index of the quantity of hydrocyanic acid being formed. Preponderance of the red cyanogen bands is associated with cyanogen chloride or bromide.

On a general view of the evidence, there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress.

I take this opportunity of thanking my colleagues, Prof. H. B. Baker and Dr. M. O. Forster, for constant help and advice.

The Capacity for Heat of Metals at Different Temperatures.

By E. H. Griffiths, Sc.D., F.R.S., and Ezer Griffiths, B.Sc., Fellow of the University of Wales.

(Received April 1,—Read May 1, 1913.)

(Abstract.)

The object of this investigation was the determination, with the closest approach to accuracy, of the specific heat of certain metals, and the changes therein caused by changes in temperature.

The work, including the necessary preliminary standardisations, has occupied our attention during the last two years and we feel unable, in this abstract, to describe with any clearness the various precautions adopted, or the somewhat elaborate process of reducing the results. We, therefore, here content ourselves with a brief indication of the methods of experiment, a statement of the results, and a short discussion of certain suggestive features which they present.

I.

The method of experiment is briefly indicated in the following numbered paragraphs:—

1. The energy was supplied electrically, and the conclusions are not dependent upon any assumption concerning the capacity for heat of bodies other than those under consideration.

2. The substances were raised across a given temperature through very small ranges of temperature (extreme limit of range, about 1·4° C.).

3. These temperature changes were measured by means of differential platinum thermometers, for which purpose these instruments are admirably adapted.

4. Large masses of the substances were used, ranging from 1 to 4 kgrm.

5. The apparatus was constructed with all the parts duplicated. The metals examined were suspended by quartz tubes in similar air-tight brass cases, which were placed side by side in a large tank containing rapidly stirred water or oil. This tank was electrically controlled with great constancy at any given temperature (θ_0).

One of the metal blocks remained at the tank temperature throughout an experiment, while the other, having been previously cooled below θ_0, was raised to a somewhat similar temperature above it by a supply of heat electrically developed in the centre of the block, the difference in the temperature between the two blocks being determined at regular intervals by means of the differential platinum thermometers.

Any changes in the surrounding conditions would, therefore, affect both blocks equally, and hence, by measuring the difference of temperature only, many possible causes of error were eliminated.

6. The equation connecting the various quantities is

$$\mathrm{MS}\,(\theta_2-\theta_1) = \frac{\mathrm{E}^2 t}{\mathrm{RJ}} \pm \mathrm{Q},$$

where M = total mass and S its specific heat, θ_1 the initial temperature and θ_2 the final temperature, E the potential difference at the extremities of the coil of resistance R, and $\mathrm{J} = 4{\cdot}184 \times 10^7$*; Q the number of thermal units lost, or gained, during time t from sources other than the electrical supply.

In these experiments the values of θ_1 and θ_2 were so arranged that Q was in every case small or negligible, and, if necessary, could be estimated with sufficient accuracy.

7. With two exceptions (Cu and Fe) the samples of metals used were supplied by Messrs. Johnson and Matthey, to whom we wish to express our sincere thanks for the trouble they have taken in the matter. Each sample was accompanied by their certificate regarding its purity.

* For a full discussion of the reasons for selecting this value of J see p. 110 of the 'Thermal Measurement of Energy,' by E. H. Griffiths (Camb. Univ. Press).

An analysis of the iron was supplied by the manufacturers, and Mr. C. T. Heycock has very kindly made an analysis of the copper.

8. Experiments on identical samples at the same temperature were repeated under very varied conditions. Two separate methods of experiment, involving different data and methods of reduction, were employed. Three different sets of differential platinum thermometers were used. The rate of heat supply was varied in the ratio of 9:1. The determination of S at a given temperature, with a particular sample, was in several cases repeated after the lapse of some months. The quartz tubes and their cover were replaced by others of different masses, etc. We were thus enabled to ascertain causes of error which would otherwise have remained undetected.

9. The results of our observations have been deduced from the actual experimental numbers and in no case from "smoothed curves."

The most serious difficulty presented by this method of experiment is that of determining the mean temperature of the block of metal when its temperature is altering. Temperature gradients must necessarily exist, since equalisation of temperature by stirring is an impossibility. The manner in which this difficulty was surmounted is described in full in the original paper.

When embarking on this investigation we proposed to extend our range of temperature to the lowest point obtainable by means of liquid air, limiting the inquiry to a study of two or three metals only.

Owing, however, to delay on the part of the contractors in the delivery of the liquid-air plant, we were compelled to postpone that portion of our investigations dealing with temperatures below 0° C. to a later date, and therefore we enlarged the scope of our inquiry so as to include the following metals, namely: aluminium, iron, copper, zinc, silver, cadmium, tin, and lead.

As the data already accumulated concerning the capacity for heat of these metals over the range 0° C. to 100° may be useful to other observers, we have seen no reason for postponing the publication of the work already completed.

II. *Statement of Results.*

In the following tables we have, in each case, inserted in Column IV the "probable error," expressed in percentages, as the resulting numbers are of a nature suitable for treatment by the "method of least squares," and this appeared to be the most concise way of indicating the extent of the discrepancies in the experimental results. This "probable error" does not, of course, include persistent errors or those present in our determinations of the various standards employed. We have, however, no reason to suppose that

such errors are of sufficient magnitude to have any appreciable effect upon our conclusions.

In order to express the relation between S and θ, many forms of equations were tried, but it was found that the mean path of the results was most closely expressed in all cases by a parabola. In Column V we give the differences (expressed in percentages) between our values as found by experiment and those deduced from the parabola given at the foot of each table. We also give the previous treatment of the metal and its analysis.

With copper an unusually large number of experiments at 0° C. were performed. Two methods were employed which involved different data. The close correspondence between the resulting numbers convinced us of the validity of both methods, and therefore, in our later work, we contented ourselves with the adoption of the more convenient, *i.e.* that which we termed the "method of intersection."

The capacity for heat of the copper case appeared as a small correction in our determinations of the specific heat of all the remaining metals. For the above reasons we made no less than 35 determinations of its specific heat at 0° C., and these were performed on different dates and under varied conditions.

In two cases, where a note of interrogation is placed after a group number, it is an indication that we regard the result as less satisfactory than usual.*

Although little weight should be attached to values thus indicated, we do not feel that we have evidence sufficient to justify us in discarding them.

The "group numbers" (Column II) do not merely indicate repetition of the same experiment, for the rate of supply of heat differed in the individual members of the group. For example, in Table I, Column II, the first group of 12 includes experiments performed with potential differences varying from 3 up to 9 Weston cells, hence the rate of heat supply was, in this group, changed in all the following proportions: 9 : 16 : 25 : 36 : 49 : 64 : 81. In no group in any of the tables are there less than three such changes. Column IV indicates the close correspondence of results obtained under such varying conditions.

With the exception of Cu and Fe, Messrs. Johnson and Matthey state that the previous history of the blocks was as follows:—"The cylinders in every instance were cast and then allowed to cool, subsequently being turned in a lathe. They were not annealed."

The weight of metal as given at the head of each table is only a rough

* We have some doubts as to the constancy of the bath temperature during these two groups.

approximation, as the mass was, in some cases, slightly altered during the series of experiments. The copper was electrolytically deposited.

Table I.—Copper.

Weight = 3392 grm. Density = 8·922.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	12	0·09084	0·03	
0	3	0·09095	0·03	
0	4	0·09098	0·05	
0	5	0·09088	0·08	
0	6	0·09079	0·03	
0	5	0·09004	0·01	
0	12	0·09081	0·04	
	Value adopted ...	0·09088		0
28·42	3	0·09230	0·06	+0·09
63·52	3	0·09365		−0·13 ?
67·32	6	0·09387	0·02	−0·07
97·4	4	0·09521	0·04	0

$$S_t = 0{\cdot}09088\,(1 + 0{\cdot}0005341\,t - 0{\cdot}00000048\,t^2).$$

Mr. C. T. Heycock writes as follows:—"Cu = 99·95 per cent. Remaining 0·05 per cent. consists of traces Pb, Fe, and a very little SiO_2. You will be correct in stating that it is of high purity."

During the above experiments at 0°, three different pairs of thermometers were employed, and two different covers to the copper case. The quartz tubes holding the block were also altered. The frequent repetition of group experiments was considered necessary in order to ascertain the effect of such changes.

With reference to the sample of aluminium employed (Table II) Messrs. Johnson and Matthey state: "Aluminium we have reason to believe to be exceptionally pure, say 99·90 per cent., with a trace of iron."

With the exception of the first group of 3, these experiments were extremely satisfactory, so much so that the fifth figure appears to have some real significance. The perfect agreement of the experimental and curve values is very noticeable.

Table II.—Aluminium.

Weight = 954 grm. Density = 2·704.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	3	0·20937	0·02	
0	11	0·20957	0·07	
	Value adopted...	0·20957		0
28·35	4	0·21471	0·02	0
51·0	7	0·21842	0·04	0
97·48	6	0·22482	0·08	0

$$S_t = 0·20957 (1 + 0·0009161\,t - 0·0000017\,t^2).$$

Table III.—Iron (ingot).

Weight = 2798 grm. Density = 7·858.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	5	0·1045	0·05	
0	3	0·1046	0·03	
	Value adopted...	0·1045		0
9·9	4	0·1061	0·11	
10·0	3	0·1059	0·02	
	Value adopted...	0·1060		0
20·5	4	0·1078	0·06	+0·22
21·5	3	0·1077	0·08	+0·10
24·5	3	0·1080	0·02	0
50·3	3	0·1105	0·08	−0·22
66·3	3	0·1112	0·24	−0·99 ?
97·5	4	0·1137	0·02	+0·10

$$S_t = 0·1045 (1 + 0·001520\,t - 0·00000617\,t^2).$$

This specimen was presented to us by the American Rolling Mill Company, Middletown, Ohio, U.S.A., who state: "Material rolled from an ingot into a billet (4 in. by 4 in.) on 'blooming mill,' billet forged into round section at blacksmith's shop. Same had no further annealing nor additional treatment other than when rolled and forged." The specimen was turned down to size in the laboratory workshop.

Analysis supplied by the manufacturers:—

Iron = 99·87.	S = 0·021.	Mn = 0·036.	O = 0·015.
	P = 0·005.	Si = trace.	N = 0·0026.
	C = 0·012.	Cu = 0·040.	H = 0·0005.

Table IV.—Zinc.

Weight = 2538 grm. Density = 7·141.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	5	0·09150	0·07	
0	3	0·09180	0·04	
	Value adopted ...	0·09176*		0
21·5	4	0·09265	0·03	−0·14
50·5	6	0·09412	0·04	+0·19
97·4	6	0·09534	0·06	
	3	0·09507	0·05	
	Value adopted ...	0·09521		−0·01
123·4	4	0·09570	0·18	+0·08

$$S_t = 0·09176\,(1 + 0·0005605\,t - 0·00000178\,t^2).$$

* Where the "value adopted" is not the mean of the numbers in Col. III in this, or other, tables, the reasons are indicated in the original paper.

Messrs. Johnson and Matthey state "approximately 99·95 per cent. zinc." The agreement between the results, on repetition at the same temperature, was less satisfactory than usual (see Column III), the extreme difference from the adopted value at 0° C. being 0·3 per cent.

Table V.—Silver.

Weight = 3733 grm. Density = 10·456.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	15	0·05563		
0	3	0·05560	0·025	
	Value adopted...	0·05560		0*
28·41	3	0·05613	0·02	0
67·40	12	0·05680	0·07	−0·07
97·44	4	0·05737	0·07	0

$$S_t = 0{\cdot}05560\,(1 + 0{\cdot}0003396\,t - 0{\cdot}000000141\,t^2).$$

Messrs. Johnson and Matthey state: "Better than 999·9 fine."

Table VI.—Cadmium.

Weight = 3070 grm. Density = 8·652.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	7	0·05481		
0	3	0·05468	0·03	
	Value adopted...	0·05475		0
28·34	4	0·05554	0·02	+0·02
54·5	6	0·05616	0·02	−0·04
97·64	5	0·05714	0·07	0

$$S_t = 0{\cdot}05475\,(1 + 0{\cdot}000520\,t - 0{\cdot}000000725\,t^2).$$

Messrs. Johnson and Matthey state: "Fully 99·75 per cent. pure, with very slight traces of iron and zinc."

Table VII.—Tin.

Weight = 2591 grm. Density = 7·292.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	14	0·05363	0·05	0
28·4	4	0·05465	0·02	+0·02
53·9	7	0·05549	0·01	−0·02
97·6	5	0·05690	0·09	+0·02

$S_t = 0·05363\,(1 + 0·0006704t - 0·000000458t^2)$.

Messrs. Johnson and Matthey state: "Probably analyse to 99·80 per cent. with trifling quantities of arsenic, lead, and iron."

Table VIII.—Lead.

Weight = 4016 grm. Density = 11·341.

I. C°.	II. No. of experiments in group.	III. S.	IV. Probable group error.	V. Difference from curve.
			per cent.	per cent.
0	10	0·030196	0·09	0
28·38	4	0·03053	0·08	0
51·0	6	0·03073	0·19	−0·16
67·4	7	0·03102	0·07	+0·19
97·45	6	0·03127	0·19	−0·03

$S_t = 0·03020\,(1 + 0·000400t - 0·00000036t^2)$.

Messrs. Johnson and Matthey state: "Approximate to 99·90 per cent., with inappreciable traces of arsenic and bismuth."

The numbers in Column IV indicate that the agreement between the individual members of a group in Table VIII is distinctly inferior to that attained with other metals. This is probably an effect of the low conductivity of lead and the consequent steepness of the thermal gradients within the cylinders.

III.

An inspection of these results will show that the curvature in the case of Al and Fe is far more marked than in the remaining metals.

The curves of Sn and Zn present certain interesting features. The specific heat of Sn at 0° appears, for reasons given elsewhere, to be exceptionally high. This may in some way be connected with the fact that Sn at temperatures not much below 0° readily assumes the "grey powder" form and it is possible, therefore, that at 0° its physical condition is an exceptional one.

The curvature in the case of Zn shows distinct alteration as the temperature approaches 100°, the rate of increase being much diminished. In consequence, in this case, we pushed our inquiry to a temperature exceeding 123° C. The results confirmed the indications observed at somewhat lower temperatures. In this connection it should be remembered that Zn becomes malleable about 120° C. and here again we have some indication of a physical cause for its abnormal behaviour.

The range of atomic weights covered by the metals enumerated above is from 27·1 (Al) to 207·1 (Pb).

At the conclusion of our experiments, we proceeded to plot our values of S at 0° C. as ordinates and the atomic weights as abscissæ. The resulting points lie very closely on the curve [deduced from the values of Al (0·2096), the mean of Cu and Zn (0·09132), and Pb (0·03020)] which is represented by

$$S = 4{\cdot}804 \times a^{-0{\cdot}95},$$

where a = atomic weight. The value of S for Sn, however, exceeds the curve value by as much as 4·6 per cent. (*i.e.*, 0·0536 as against 0·0512).

We have endeavoured to ascertain how nearly the values of S obtained from this curve are in harmony with the experimental results of observers in the case of elements not examined by us. In a large number, no satisfactory information is procurable and, where information exists, it is difficult to estimate its true value. Again, few observers have used a range of temperature including 0° C., and, in such cases, we have had to reduce their results to 0° by means of the values given by them at other temperatures, assuming the changes to be of a linear order. In our full paper we have stated, in every case, the authority and the data by which we ascertained the most probable values at 0° C.

The following table shows the results of the investigation:—

Column I gives the percentage difference between the calculated and the experimental values (a positive sign indicating the latter as the greater) in those cases where the difference does not exceed 3 per cent. In the case of

all gases, however, the experimental values have been doubled before making the comparison.

Column II. Elements whose differences lie between 3 and 16 per cent. Of these, however, we do not consider the values of N, Na, and K to be sufficiently established to warrant any conclusions, and we may state that, in order to test this point, we are now engaged in the determination of the specific heat of Na.

Column III.* Elements whose experimental values differ so greatly from the calculated as to exclude the possibility of agreement. A couple of curious coincidences, however, present themselves. The calculated value of C (0·453) is almost exactly four times that of the diamond (0·113).

The mean value for amorphous B (0·250) is very closely half the calculated.

Table IX.

Col. I.				Col. II.		Col. III.*		
	per cent.		per cent.		per cent.		Calculated.	Experimental.
H	0	As	−2·3	He	+15·0			
Li	+2·0	Kr	−0·7	N	−10			
O	−1·2	Pd	0	Cl	+ 6	B	0·492	0·250
Mg	+0·9	Ag	−1·2	Na	+16	C	0·453	0·113
Al	0	Cd	+1·1	K	+11	Si	0·201	0·177
P	+2·2	Sb	−1·6	Sn	+ 4·6	Hg	0·0313	0·0335* 0·0314†
A	+1·9	Pt	−1·6	Cs	+ 4·0?			
Fe	−0·5	Tl	+0·3					
Ni	0	Pb	−0·3					
Co	−1	Bi	−0·6					
Cu	−2·2	U	+3·0?					
Zn	+1·3							
Sum of differences = −0·5.						* Liquid.		† Solid.

We are aware of the serious difficulties in the way of accepting any such relation as that given by the above equation between the atomic weights and specific heats at an arbitrary temperature such as 0° C. It is, however, possible that the large majority of elements are in a stable condition at that temperature, and, if such is the case, some definite connection may exist between their atomic weights and specific heats. However this may be, one thing is evident, viz., that the curve $S = 4{\cdot}804 \times a^{-0{\cdot}95}$† gives, throughout the whole range of atomic weights, values of S (2S in the case

* In Column III the actual numbers, instead of percentage differences, are given.

† The expression "Atomic heat $= 4{\cdot}804 \times a^{0{\cdot}05}$" is evidently an alternative manner of expressing the same relation.

of gases) which, in a very large majority of cases, are within 2 per cent. of the most probable values.*

It has already been pointed out that the curvature of the S, θ curve in the case of Al and Fe differs markedly from that of the remaining metals on our list. If we take those six remaining metals (Cu, Zn, Ag, Cd, Sn, and Pb), and, from the parabolic formulæ given *supra*, deduce the point of intersection with the ordinate at -273, and, assuming the resulting values of S, find their atomic heats at absolute zero, we obtain as the mean of our results the number 4·813, their differences from the mean being surprisingly small, when we consider the effect of any error in the values of the coefficients over the range 0° to 100° C. If then, assuming the values of S at $-273°$ given by $a \times S = 4{\cdot}813$, and the experimental values of S at 0° and 100°, we construct the resulting parabolas and ascertain the differences between the experimental and the calculated values at the various points experimentally determined by us, we find that in no instance does the difference exceed 0·3 per cent., and that it is, in most cases, much less.

The remarkable approximation between the hypothetical value of the atomic heat at 0° C. of a body with atomic weight 1 (4·804) and the likewise hypothetical value of the atomic heat of the group of metals at absolute zero (4·813) is probably a coincidence, but may possibly be of real significance.

* If we assume the value of Dulong and Petit's constant as 6·25, the deduced values for the elements in Column I would, in some cases, differ from the experimental ones by as much as 30 per cent.

On Fourier Series and Functions of Bounded Variation.

By Prof. W. H. Young, Sc.D., F.R.S.

(Received April 10,—Read June 19, 1913.)

§ 1. In a previous communication to the Society I have pointed out that the succession of constants obtained by multiplying together two successions of Fourier constants in the manner which naturally suggests itself is a succession of Fourier constants, and I have discussed the summability of the function with which the new constants are associated. We may express the matter in another way by saying that I have shown that the use of the Fourier constants of an even function $g(x)$ as convergence factors in the Fourier series of a function $f(x)$ changes the latter series into a series which is still a Fourier series, while the summability of the function which is associated with the new series is increased. The use of the Fourier constants of an odd function as convergence factors, on the other hand, has the effect of changing the allied series of the Fourier series of $f(x)$ into a Fourier series, even when the allied series is not itself a Fourier series.

It at once suggests itself that the former of the two statements in this form of the result is not the most that can be said. Indeed, the series, whose general term is $\cos nx$, and whose coefficients are accordingly unity, may clearly take the place of the Fourier series of $g(x)$, although it is not a Fourier series. On the other hand, it is the derived series of the Fourier series of a function of bounded variation, which is, moreover, odd. We are thus led to ask ourselves whether this is not the trivial case of a general theorem. In the present communication I propose to show, among other things, that the answer to this question is in the affirmative. The following theorems are, in fact, true:—

If the coefficients of the derived series of a Fourier series of an odd function of bounded variation be used as convergence factors, the Fourier series of a general summable function will remain the Fourier series of a summable function, while the degree of summability of the function will in general be unaltered. On the other hand, if the function of bounded variation used be even, the corresponding convergence factors obtained by deriving its Fourier series will have the effect of transforming the allied series of a Fourier series into the Fourier series of a function having the same degree of summability as the function corresponding to the original Fourier series.

These results appear to me to possess of themselves sufficient interest to justify my communicating them to the Society. Apart, however, from their

intrinsic interest, the method by which I have been led to obtain them is, I think, at once suggestive and instructive. In germ this method has already been employed by Stieltjes. Properly handled and suitably developed, it constitutes a very effective tool in dealing with some of the finer distinctions in the Theory of Functions of a Real Variable. For this purpose, however, we require to introduce the notion of the summability of a function $f(x)$ with respect to a function of bounded variation $g(x)$, and not merely, as Stieltjes does, to employ an analytical expression, which may be interpreted as the Riemann integral of a continuous function taken with respect to a monotone function. Moreover, we require to have a theory of integration with respect to a function of bounded variation which shall correspond to that of integration with respect to the independent variable, such as I have exposed in a recent communication to the Society.* When this has been done we may integrate sequences and successions with respect to any assigned function of bounded variation, whether continuous or not, under conditions which are analogous to those in the known theory.

In particular, we have a theory of the integration of Fourier series term by term with respect to a function of bounded variation of the most general type. We are thus led to a variety of results of interest, and, among others, to those I have stated above. I have not attempted to give a complete account of the theory, but I have thought it well to take the opportunity to enunciate and give indications of proof of some of the connected results so obtained. Among these may be mentioned the one which states that if a trigonometrical series has the property that its integrated series converges everywhere boundedly, then term-by-term integration of the trigonometrical series is allowable after it has been multiplied by any function of bounded variation whatever, the sum of the latter integrated series being expressible in terms of the integral of the function of bounded variation with respect to

* *Added June*, 1913.—In the order of ideas there indicated various slightly different but equivalent modes of treatment are possible. If we start with simple l and u functions and define, as we evidently may content ourselves with doing, their integrals with respect to a monotone increasing function $g(x)$, special attention must be paid to the discontinuities of $g(x)$, unless we hypothecate that the simple functions are so chosen that none of their discontinuities coincide with those of $g(x)$. We may also, if we please, start with the integral of a continuous function, using for this purpose the formula of Stieltjes; this corresponds to the treatment suggested in my paper, "On a New Method in the Theory of Integration," cited below. I am, by request, writing out a systematic account of these matters, and propose to present the paper containing it to the London Mathematical Society. All turns on the use of monotone sequences. Another, but far less intuitive form of treatment, has been briefly indicated by Lebesgue. He employs, but evidently with great reluctance, the process of change of the independent variable. See H. Lebesgue, 'Comptes Rendus,' 1909.

the function which is the sum of the integrated trigonometrical series itself. Again, it appears that the coefficients of the derived series of the Fourier series of respectively an odd and an even function of bounded variation, when employed as convergence factors, change the Fourier series of a continuous function and its allied series into the Fourier series of continuous functions.

The theory of the summability of a function with respect to a function of bounded variation is, it will be noted, only part of a still larger theory. Even Stieltjes was led to consider integration with respect to a continuous function, owing to the necessity of formulating a theorem of integration by parts. In general, however, the generalisation in this direction involves difficulties of a nature analogous to those which arise when we are dealing with non-absolutely convergent integration with respect to the independent variable. I do not propose, therefore, in the present communication, to enter on these matters.

§ 2. It will not be necessary on this occasion to enter into details with regard to the theory of integration with respect to a function, and in particular with respect to a function of bounded variation. It will be evident that a function which is summable may, or may not, be summable with respect to an assigned function of bounded variation, and a sequence or succession which is integrable term by term may, or may not, remain integrable term by term when the integration is with respect to a function of bounded variation. The rules, however, which enable us to recognise such possibilities in the general case are usually completely analogous to the known ones in the special case. Thus we have merely to remark that the repeated integral with respect to two monotone increasing functions of a positive function is necessarily independent of the order in which the integration is performed, to see that, if $g(t)$ is any function of bounded variation whatever, and $f(t)$ is any summable function, the integral of $f(x+t)$ with respect to $g(t)$ certainly exists except for a set of values of x of content zero. Using Stieltjes' notation, and interpreting it in the extended sense above explained, we may accordingly write

$$\int_a^x dx \int f(x+t)\,dg(t) = \int \{\mathrm{F}(x+t)-\mathrm{F}(x-t)\}\,dg(t), \qquad (1)$$

where $\mathrm{F}(x)$ is an indefinite integral of $f(x)$.

We thus see that the right-hand side of (1) is an integral with respect to x, and that the inside integral on the left certainly exists, except at a set of content zero, while it constitutes a summable function of x.

§ 3. Again we see immediately that sequences that converge uniformly can certainly be integrated with respect to any function of bounded variation.

In fact let $f_n(x)$ be the general term of a sequence which approaches $f(x)$ uniformly. Then it is plain that $\int [f_n(t)-f(t)]\, dg(t)$ has, as $n\to\infty$, the unique limit zero. For we can find an n so that $|f_n(t)-f(t)|$ is less than e, for all points t in the interval of integration, and we may suppose $g(t)$ expressed as the difference of two positive monotone functions. Each of the corresponding integrals will then be less than a certain finite multiple of e, and is therefore as small as we please. Hence the limit of our integral, as $n\to\infty$, is zero.

But, more generally, it is sufficient that the sequence should converge boundedly for the same to be true. To see this we have, in fact, merely to retrace the steps of the reasoning by which, in a recent communication to the Society, I showed that the process is allowable when integration is taken in the new generalised sense there explained. *Mutatis mutandis* the whole argument applies.

§ 4. Let $f(x) \sim \Sigma(a_n \cos nx + b_n \sin nx)$, and consider the series

$$\Sigma\alpha_n(a_n \cos nx + b_n \sin nx), \tag{2}$$

where

$$\alpha_n = \frac{1}{\pi}\int_{-\pi}^{\pi} n \sin nt\, g(t)\, dt, \tag{3}$$

$g(t)$ being an odd function of bounded variation, so that α_n is the typical coefficient of the trigonometrical series got by differentiating term by term the Fourier series of $g(t)$.

We are about to prove that the series (2) is the Fourier series of the following function—

$$\phi(x) = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\, dg(t). \tag{4}$$

We have by (4)

$$\frac{1}{\pi}\int_{-\pi}^{\pi}\phi(x)\cos nx\, dx = \frac{1}{\pi}\int_{-\pi}^{\pi}\left(\frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\cos nx\, dx\right) dg(t). \tag{5}$$

In fact, change of order of integration with respect to $g(t)$ and x is permitted when the factor $\cos nx$ is omitted, and is therefore, by a theorem, analogous to a known theorem in ordinary repeated integration, allowable when $\cos nx$ is present. Now the inside integral on the right-hand side of (5) is evidently equal to

$$a_n \cos nt + b_n \sin nt.$$

We can, in the further evaluation of the right-hand side of (5), almost without leaving the realm of Stieltjes' ideas, employ an obviously allowable generalisation of the ordinary theory of integration by parts. The term $b_n \sin nt$ evidently contributes nothing to the result, since $g(t)$ is odd; and

since $g(t)$ vanishes at the limits of integration* with respect to t, of the two parts involving a_n, one vanishes identically. Hence (5) becomes

$$\frac{1}{\pi}\int_{-\pi}^{\pi}\phi(x)\cos nx\,dx = \frac{1}{\pi}a_n\int_{-\pi}^{\pi}g(t)\,n\sin nt\,dt = a_n\alpha_n. \tag{6}$$

Similarly
$$\frac{1}{\pi}\int_{-\pi}^{\pi}\phi(x)\sin nx = b_n\alpha_n. \tag{7}$$

The equations (6) and (7) show that the series (2) has the Fourier form, and that the corresponding function is $\phi(x)$, as was stated.

§ 5. Next consider the series

$$\Sigma\beta_n(-b_n\cos nx + a_n\sin nx), \tag{8}$$

where
$$\beta_n = \frac{1}{\pi}\int_{-\pi}^{\pi}n\cos nt\,h(t)\,dt, \tag{9}$$

$h(t)$ being an even function of bounded variation, so that $-\beta_n$ is the typical coefficient of the trigonometrical series got by differentiating term by term the Fourier series of $h(t)$.

We are about to prove that the series (8) is the Fourier series of the following function—

$$\psi(x) = \frac{1}{\pi}\int_{-\pi}^{\pi}f(x+t)\,dh(t). \tag{10}$$

We have, as before,

$$\begin{aligned}\frac{1}{\pi}\int_{-\pi}^{\pi}\psi(x)\cos nx\,dx &= \frac{1}{\pi}\int_{-\pi}^{\pi}\left(\frac{1}{\pi}\int_{-\pi}^{\pi}f(x+t)\cos nx\,dx\right)dh(t)\\ &= \frac{1}{\pi}\int_{-\pi}^{\pi}(a_n\cos nt + b_n\sin nt)\,dh(t) = \frac{1}{\pi}\int_{-\pi}^{\pi}b_n\sin nt\,dh(t)\\ &= -b_n\beta_n,\end{aligned} \tag{11}$$

$$\begin{aligned}\frac{1}{\pi}\int_{-\pi}^{\pi}\psi(x)\sin nx\,dx &= \frac{1}{\pi}\int_{-\pi}^{\pi}\left(\frac{1}{\pi}\int_{-\pi}^{\pi}f(x+t)\sin nx\,dx\right)dh(t)\\ &= \frac{1}{\pi}\int_{-\pi}^{\pi}(b_n\cos nt - a_n\sin nt)\,dh(t) = -\frac{1}{\pi}\int_{-\pi}^{\pi}a_n\sin nt\,dh(t)\\ &= a_n\beta_n.\end{aligned} \tag{12}$$

The equations (11) and (12) show that the series (8) has the Fourier form, and that the corresponding function is $\psi(x)$.

§ 6. We may next discuss the summability of the functions $\phi(x)$ and $\psi(x)$, and the mode in which this depends on the summability of $f(t)$. There is no difficulty in seeing that both these functions belong in general to the

* In fact, as we suppose $g(x)$ periodic and odd, its values when $x = -\pi$ and $x = +\pi$ must be both zero.

same class of functions as $f(x)$. If we consider in particular the case in which the $(1+p)$th power of $f(x)$ is summable, we have only to use the inequality

$$(\int u\,dv)^{1+p} \leq \int u^{1+p}dv\,.\,(\int dv)^p,$$

where u and v are any positive functions of the independent variable x.

More generally we may use the inequality

$$Q\left(\frac{\int u\,dv}{\int dv}\right) \leq \frac{\int Q(u)\,dv}{\int dv},$$

where $Q(t)$ is the indefinite integral of any positive function whose differential coefficient is positive (>0).* This inequality may evidently be proved in a manner analogous to that used in proving the corresponding inequality† when v is itself the independent variable, with whose limits of integration we are concerned.

Putting then $u = f(x+t)$ and v equal to the total variation of $g(t)$, or $h(t)$ as the case may be, and taking t to be the independent variable, the required results immediately follow.

§ 7. It may also be remarked that the corresponding reasoning shows that the effect of integrating the Fourier series of a function of bounded variation, and its allied series, with respect to an odd function of bounded variation and an even function of bounded variation respectively is, in the former case, to preserve the character of being the Fourier series of such a function; and, in the latter case, to transform the allied series into such a Fourier series. Or, as we may otherwise express it, the convergence factors α_n and β_n have these effects respectively.

§ 8. If, on the other hand, we perform the process of integration with respect to a function of bounded variation on the Fourier series of a continuous function, we easily prove that the following result holds good:—

If α_n and β_n are the typical coefficients of the derived series of the Fourier series of respectively an odd and an even function of bounded variation, then the convergence factor α_n transforms the Fourier series of a continuous function into the Fourier series of a continuous function, while the convergence factor β_n changes the allied series of the Fourier series of such a function into the Fourier series of a continuous function.

In fact, the argument is precisely the same as that employed in §§ 4 and 5,

* "On Classes of Summable Functions and their Fourier Series," 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 227.

† "On the New Theory of Integration," 'Roy. Soc. Proc.,' 1912, A, vol. 88; see also "On a New Method in the Theory of Integration," 'Lond. Math. Soc. Proc.,' 1910, Ser. 2, vol. 9, pp. 15–50.

and shows that the functions with which these series, as Fourier series, are associated are respectively

$$\phi(x) = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\, dg(t) \quad \text{and} \quad \psi(x) = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\, dh(t),$$

where g and h are respectively the odd and even functions of bounded variation. The theorem stated follows immediately from the known property of a continuous function of being uniformly continuous. We may indeed find a quantity η, independent of t (and of x), such that for this and all smaller values,

$$| f(x+t+\eta) - f(x+t) |$$

is less than a fixed quantity e, as small as we please.

Hence, for $0 \leq \delta \leq \eta$,

$$| \phi(x+\delta) - \phi(x) | \leq \frac{e}{\pi}\int_{-\pi}^{\pi} | dg(t) | ,$$

which, as the total variation of $g(t)$ is finite, proves the continuity of $\phi(x)$. Similarly, $\psi(x)$ is seen to be continuous.

Or, more simply, we may remark that the sequence $f(x+t+h)$ converges uniformly to $f(x+t)$ as $h \to 0$, whence the required result follows by § 3.

§ 9. Finally we shall prove the following theorem, which, it will be seen, is of a slightly different type.

If a_n and b_n are the typical Fourier constants of a function $f(x)$ of bounded variation, and A_n and B_n the typical coefficients of a trigonometrical series whose integrated series converges boundedly to $G(x)$, then the series whose general term is

$$(a_n A_n + b_n B_n) \cos nx - (a_n B_n - b_n A_n) \sin nx$$

converges boundedly and has for sum

$$\frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\, dG(t).$$

To prove this we have only to employ the theorem to which allusion has been made in the last few lines of § 3.

In fact, since the series whose general term is

$$\frac{1}{n}(A_n \sin nx - B_n \cos nx)$$

converges boundedly to $G(x)$, it is the Fourier series of $G(x)$, and to prove the result we have merely to integrate term by term the Fourier series of $G(t-x)$ with respect to $f(t)$. We shall then get the right-hand side of the equation to be proved with its sign changed on the right of our equation, while on the

left we shall have the expression $\frac{1}{\pi}\int_{-\pi}^{\pi} G(t-x)\, df(t)$. Carrying out the integration in this last expression by parts, and remembering that G and f are both periodic, and in particular are supposed at have at the one limit of integration the same values as at the other limit, the required result follows.

§ 10. The result just obtained appears to be not without importance, more especially in view of the circumstances that, though it is not known when we may safely assert that the allied series of a Fourier series is itself a Fourier series, we do know that the integrated series of the allied series of a Fourier series converges boundedly, and even uniformly, in a large variety of cases.

It will be seen that all has turned in the present theory on the fact that a function of bounded variation is not necessarily an integral. In the cases which most naturally present themselves the function is only not an integral because it has one or more finite discontinuities. In the best known example of the Fourier series of a function of bounded variation, viz. the series whose general term is $\sin nx/n$, this is precisely what occurs. We may verify our results in this trivial case by showing that the integral of a function $f(t)$ which has only discontinuities of the first kind with respect to the function $g(t)$ of bounded variation which is the sum of the series $\Sigma \sin nx/n$, is the original function, or, more precisely,

$$\frac{1}{\pi}\int_{-\pi}^{\pi} f(x+t)\, dg(t) = \tfrac{1}{2}\{f(x+0)+f(x-0)\}.$$

The difference in the behaviour of a Fourier series and its allied series corresponds to the fact that the series whose general term is $\cos nx/n$ is not the Fourier series of a function of bounded variation. It would be of interest to obtain the simplest cosine series having the property of being the Fourier series of a discontinuous function of bounded variation. A knowledge of such a series would give us a number of interesting results, which would follow as immediate consequences of the reasoning we have here employed.

On a Condition that a Trigonometrical Series should have a Certain Form.

By Prof. W. H. YOUNG, Sc.D., F.R.S.

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§ 1. In a recent communication to the Society I have illustrated the fact that the derived series of the Fourier series of functions of bounded variation play a definite part in the theory of Fourier series. Some of the more interesting theorems in that theory can only be stated in all their generality when the coefficients of such derived series take the place of the Fourier constants of a function. I have also recently shown that Lebesgue's theorem, whether in its original or in its extended form, with regard to the usual convergence of a Fourier series when summed in the Cesàro manner is equally true for the derived series of Fourier series of functions of bounded variation. I have also pointed out that, in considering the effect of all known convergence factors in producing usual convergence, it is immaterial whether the series considered be a Fourier series, or such a derived series.

We are thus led to regard the derived series of the Fourier series of functions of bounded variation as a kind of pseudo-Fourier series, possessing properties which are identical with or analogous to those of Fourier series, properly so-called. In particular we are led to ask ourselves what is the necessary and sufficient condition that a trigonometrical series should have the form in question. One answer is of course immediate. The integrated series must converge to a function of bounded variation. This is merely a statement in slightly different language of the property in question. We require a condition of a simpler formal character, one which does not require us to solve the difficult problem as to whether an assigned trigonometrical series not only converges but also has for sum a function of bounded variation.

I have already indicated the corresponding answer in the case when the trigonometrical series is required to be the Fourier series of a function of a particular class. If the class be the class of functions whose $(1+p)$th power is summable, this condition is that

$$\int_{-\pi}^{\pi} |f_n(x)|^{1+p} dx$$

should be a bounded function of n, where $f_n(x)$ denotes the nth Cesàro partial summation of the series considered.

In the present communication I propose to show that the necessary and sufficient condition that a trigonometrical series should be the derived series of the Fourier series of a function of bounded variation is that

$$\int_{-\pi}^{\pi} |f_n(x)|\, dx$$

should be a bounded function of n.

This result seems to me to be worthy of the attention of the Society for various reasons. It not only illustrates the fact that a function, about which all that we know is that it is summable, is necessarily more than merely summable, but it of itself justifies our regarding such derived series as having their definite place in our theory. Moreover, the method by which it is obtained has an interest of its own. It involves the consideration of bounded successions of integrals of positive functions, and we are led by the exigencies of the reasoning to conclude *a priori* the probability of such successions of integrals containing sequences. It was, in fact, in this way that I was led to remark that this result is immediately deducible from reasoning which I had already employed. We have, in fact, the following theorem :—If the integrands of a bounded succession of integrals are bounded below in their ensemble, there is in every sub-succession of the succession of the integrals a sequence which converges to a lower semi-continuous upper semi-integral, in other words, to an asymmetrically continuous function of bounded variation of a certain type.

The cases in which we can assert that an oscillating succession contains a sequence are very few in number. Almost the only one known is that discovered by Arzelà, and which, in the extended and modified form given to it by myself, requires the condition of uniform and homogeneous oscillation on one side at least. Such successions have come to have a considerable theoretical importance in the abstract theory of sets, as well as in the applications to the theory of functions of a real variable.

It is noteworthy that in the present instance, though this does not come out in the proof, there is uniform and homogeneous oscillation on the left. This follows indeed from a fact that I have long ago signalised, viz., that the non-uniformity of the oscillation of a succession of monotone continuous functions is always visible.

With regard to the main result of the paper it will be noted that it gives us at the same time the necessary and sufficient condition that a trigonometrical series should be the Fourier series of a function of bounded variation.

It may finally be remarked that if instead of expressing the Fourier coefficients of the Fourier series as ordinary integrals involving the function

itself in the integrand, we express them in terms of integrals with respect to the indefinite integral of that function, the form thus given to the Fourier series is identical with the corresponding one for the derived series of a Fourier series, the only difference being that the function with respect to which the integration is to be performed is in the latter case a function of bounded variation which is not in general an integral.

§ 2. We first prove the theorem with respect to successions of integrals to which reference has been made.

Theorem.—*If a succession of integrals of functions which are bounded below (above) in their ensemble oscillates boundedly, there is in every sub-succession a sequence of the integrals, converging to a lower (upper) semi-continuous upper (lower) semi-integral.*

It will be sufficient to prove the former of the two alternative statements in the theorem. Since the succession of integrals is bounded and that of the integrands $f_n(x)$ is bounded below, the latter succession is semi-integrable below; therefore all the upper functions and all the lower functions of the succession of integrals are upper semi-integrals.*

Again, from the fact that the succession $f_n(x)$ is bounded below, it follows that $\int_E f_n(x)\,dx$ has no negative double limit, as $n \to \infty$ and $E \to 0$, and accordingly that the succession of integrals oscillates uniformly and homogeneously below.† Hence all the upper and all the lower functions of the succession of integrals are lower semi-continuous functions.

Now an upper semi-integral is the sum of an integral, which is a continuous function, and a monotone increasing function, which, in our case, is accordingly a lower semi-continuous function, and therefore continuous on the left.

But I have elsewhere‡ proved that, if all the upper, or all the lower, functions of a succession are continuous on one side at least, the same at each point for all such upper or lower limiting functions, then a sequence of the functions can be found having an unique limiting function. In our case the functions are the integrals $\int f_n(x)\,dx$, so that, by this theorem, we can find a succession of integers $n_1, n_2, \ldots$, such that $\int f_{n_i}(x)\,dx$ converges, as $i \to \infty$, to an unique limiting function, which, being one of the lower and upper limiting functions of the succession of integrals, is, by what has been

* W. H. Young, "Semi-integrals and Oscillating Successions of Functions," 'Lond. Math. Soc. Proc.,' 1910, Ser. 2, vol. 9, pp. 300–301, §§ 15–16.

† W. H. Young, "Successions of Integrals and Fourier Series," *ibid.*, 1912, vol. 11, p. 51.

‡ W. H. Young, "On Homogeneous Oscillation of Successions of Functions," *ibid.* 1912, vol. 8, p. 356, Cor. 4.

pointed out, a lower semi-continuous upper semi-integral, and therefore continuous on the left.

Since the succession $f_n(x)$ may equally well be any sub-succession of the given succession, this proves the theorem in the case when the integrands are bounded below in their ensemble. Similarly the alternative case may be proved.

§ 3. We are now able to obtain the result which forms the main object of this communication.

Theorem.—*The necessary and sufficient condition for a trigonometrical series*

$$\sum_{m=1} (a_m \cos mx + b_m \sin mx) \tag{1}$$

to be the derived series of the Fourier series of a function of bounded variation is that

$$\int_{-\pi}^{\pi} | f_n(x) | \, dx \leqq C,$$

where C *is a finite constant independent of* n, *and* $f_n(x)$ *is the Cesàro partial summation of the series* (1).

First, to prove the sufficiency of the condition.

Since $\int_{-\pi}^{x} |f_n(x)| \, dx$ is a bounded function of (n, x), the same is true of $\int_{-\pi}^{x} \{ |f_n(x)| + f_n(x)\} \, dx$. The integrands of these two integrals being positive, we can apply to each of them the theorem of § 2. Thus we can find such a succession of integers n_1', n_2', ..., that, for this succession of values of n, the first of the integrals describes a sequence. The corresponding values of the second integral form a sub-succession to which we again apply the theorem, and find a succession of integers n_1, n_2, ..., from among n_1', n_2', ..., so that as n describes these values, the second integral describes a sequence. Therefore as n describes the succession n_1, n_2, ..., both the integrals describe sequences, and therefore their difference, namely $\int_{-\pi}^{x} f_n(x) \, dx$ also describes a sequence. By § 2, the limiting functions of the two first sequences are semi-integrals, and therefore functions of bounded variation. Hence the limiting function of the last sequence, say $g(x)$, is a function of bounded variation, and we have

$$g(x) = \operatorname*{Lt}_{r \to \infty} \int_{-\pi}^{x} f_{n_r}(x) \, dx = \operatorname*{Lt}_{r \to \infty} F_{n_r}(x), \text{ say}, \tag{2}$$

where
$$F_{n_r}(x) = \int_{-\pi}^{x} \left\{ \sum_{i=1}^{i=n_r} \left(1 - \frac{i-1}{n_r}\right) (a_i \cos ix + b_i \sin ix) \right\}$$
$$= \sum_{i=1}^{i=n_r} \left(1 - \frac{i-1}{n_r}\right) (a_i \sin ix - b_i \cos ix - b_i)/i. \tag{3}$$

Since $F_{n_r}(x)$ is a bounded function of (n, x), we may integrate (2) term by term after multiplying both sides by $\cos mx$. Thus

$$\frac{1}{\pi}\int_{-\pi}^{\pi} g(x)\cos mx\,dx = \underset{r\to\infty}{\mathrm{Lt}}\left(-1+\frac{m-1}{n_r}\right) b_m/m = -b_m/m. \tag{4}$$

Similarly, multiplying (2) by $\sin mx$ and integrating term by term

$$\frac{1}{\pi}\int_{-\pi}^{\pi} g(x)\sin mx\,dx = a_m/m. \tag{5}$$

From (4) and (5),

$$g(x) \sim \text{const.} + \sum_{m=1} \{-b_m \cos mx + a_m \sin mx\}/m.$$

This shows that our trigonometrical series (1) is the derived series of the Fourier series of the function $g(x)$ of bounded variation, provided the given condition is satisfied. The condition is therefore sufficient. Next to prove that it is necessary.

Let $g(x)$ be the function of bounded variation, corresponding to which the series (1) is the derived series of the Fourier series. Since $g(x)$ is the difference of two monotone increasing functions, and therefore

$$f_n(x) = f_{n,1}(x) - f_{n,2}(x),$$

where $f_{n,1}(x)$ and $f_{n,2}(x)$ are the Cesàro partial summations of the derived series of the Fourier series of these monotone increasing functions, it is only necessary to prove the necessity of the condition when the function of bounded variation is a monotone increasing function.

Now, when $g(x)$ is a monotone increasing function, $f_n(x)$ is positive, for

$$f_n(x) = \frac{1}{2n\pi}\int_{-\pi}^{\pi} \frac{\sin^2 \frac{1}{2}n(x-t)}{\sin^2 \frac{1}{2}(x-t)}\,dg(t).$$

Therefore, in this case $\int_{-\pi}^{\pi} |f_n(x)|\,dx$ is $\int_{-\pi}^{\pi} f_n(x)\,dx$, and is given by the right-hand side of (3). Denoting by $T_n(x)$ the Cesàro partial summation of the Fourier series of which our series is the derived series, we have, therefore,

$$\int_{-\pi}^{\pi} f_n(x)\,dx = T_n(x) - T_n(-\pi) \leq C,$$

where C is the upper bound of the Cesàro partial summations of the Fourier series of $g(x)$, which, as is known,* converges boundedly in the Cesàro manner, since $g(x)$ has bounded variation. Thus the condition is necessary when $g(x)$ is monotone increasing, and therefore also, in the general case, when $g(x)$ is a function of bounded variation.

* W. H. Young, "On the Integration of Fourier Series," 'Lond. Math. Soc. Proc.,' 1910, Ser. 2, vol. 9, pp. 452–453, § 3.

§ 4. Bearing in mind what has been said in § 1, it will be seen that the following theorem completes the set of tests of the type considered:—

Theorem.—*The necessary and sufficient condition that a given trigonometrical series should be the Fourier series of a bounded function is that* $|f_n(x)| \leq \mathrm{B}$ *for all values of* n *and* x, B *being a finite constant.*

That this condition is necessary is evident from mere inspection of the usual expression for $f_n(x)$. That it is sufficient follows from reasoning of a similar but simpler character to that employed in the analogous theorems.

In fact, if $f_n(x)$ is a bounded function of (n, x), the integrated series necessarily oscillates uniformly and homogeneously when summed in the Cesàro manner, index unity. Accordingly, a sequence of these Cesàro partial summations can be found converging to an integral, since $\int_{\mathrm{E}} f_n(x)$ has the unique double limit zero when $\mathrm{E} \to 0$, $n \to \infty$. In other words, we have

$$\int_a^x f(x)\,dx = \underset{r\to\infty}{\mathrm{Lt}} \int_a^x f_{n_r}(x)\,dx,$$

where, moreover, $f(x)$ is a certain bounded function.* Multiplying both sides of this equation by $\cos mx$, or by $\sin mx$, and integrating term by term, we see that the integrated series is a Fourier series, having $\mathrm{F}(x)$ for corresponding function; that is, the integrated series is the Fourier series of the integral of a bounded function, whence the theorem follows.

* "Successions of Integrals and Fourier Series," *loc. cit.*, p. 31.

On a Method of Measuring the Viscosity of the Vapours of Volatile Liquids, with an Application to Bromine.

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The determination of several of the physical properties of the halogens is rendered difficult by reason of their great chemical activity. This is particularly the case where pressure measurements are involved, it being almost impossible to choose a gauge fluid which is unacted upon by these elements. It was in order to surmount this difficulty that the following method was devised, and this paper deals with its application to the determination of the viscosity of gaseous bromine at various temperatures. It will be seen that in the apparatus used the only possibility of chemical action is between the bromine and the glass, and the author has been given to understand that this does not occur to any appreciable extent. Although originally designed for the purpose of avoiding chemical action, the method to be described appears to form a very suitable means of determining the viscosity of the vapour of any volatile liquid, the only data required being the saturation vapour pressures over a small temperature range and the densities of the liquid over the same range.

Method of Experiment.

The method is based upon O. E. Meyer's transpiration formula, and the modifications of the older methods consist in the special devices adopted for estimating the pressures at the two ends of the capillary tube, and for measuring the quantity of gas passing through it. Fig. 1 shows an ideal form of the apparatus, which will suffice to indicate the principles involved. A and B are two glass bulbs connected by a capillary tube, and the

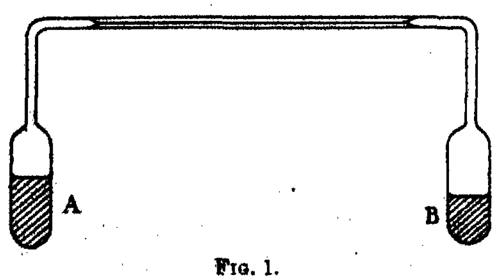

FIG. 1.

apparatus contains nothing but the liquid and its vapour. If A is maintained at a higher temperature than B, the liquid will evaporate in A and condense in B. With a capillary tube of sufficiently narrow bore it would obviously be possible to restrict the rate of flow so as to secure that the pressures in A and B were the saturation vapour pressures at the temperatures of the respective enclosures. The mass of gas traversing the capillary tube in a specified time could be estimated either from the volume of liquid disappearing from A or from that condensing in B, provided that the density of the liquid be known. All the data for measuring the viscosity of the vapour would then be available, and by maintaining the capillary tube at various temperatures higher than that of A (this to secure that no condensation should occur elsewhere than in B), the viscosities at those temperatures could be determined. Further, the apparatus being symmetrical, measurements in alternate directions could be performed successively.

In practice, however, the experiment is scarcely so simple as this. Owing to the smallness of the volume of liquid corresponding to a large volume of vapour, it is clearly desirable that the vessels A and B should not be bulbs, but should take the form of graduated tubes, narrow in bore, although not of course, comparable in this respect with the capillary itself. When this is the case it is found that with a capillary whose bore is of sufficient size to permit of accurate measurement, the pressures at the two ends are no longer equal to the saturation vapour pressures for the temperatures of the baths in which A and B are immersed. This is, of course, to be attributed to the fact that when the rate of distillation through the capillary is large, heat can neither enter A nor leave B rapidly enough to secure equilibrium between the liquid and its vapour. The consequence is that the pressure in A is less than, and that in B greater than the corresponding saturation pressures, and in order to find the true pressures means have to be adopted for estimating the above differences. A consideration of the diagram of the apparatus actually used will show how this was achieved. It will be seen (fig. 2) that the vessels A and B are U-tubes, sealed at the ends remote from the capillary. They are enclosed in water baths, the temperatures of which differ by several degrees. Let us suppose that that containing A is at the higher temperature. The temperature of the bath containing A must be lower than that of any other part of the apparatus except B, and, with this restriction, the temperature of the bath C containing the capillary tube may be maintained at the value at which it is desired to determine the viscosity of the vapour. The vapour which evaporates from A passes through the glass spiral *a* in order that it may be raised to the desired

temperature before entering the capillary. After emerging from the other end it is eventually condensed to liquid in B.

Now let us consider what happens in the closed limbs of the vessels A and B. The variations of level to which the liquid is subject in these limbs is not such as to involve appreciable evaporation or condensation

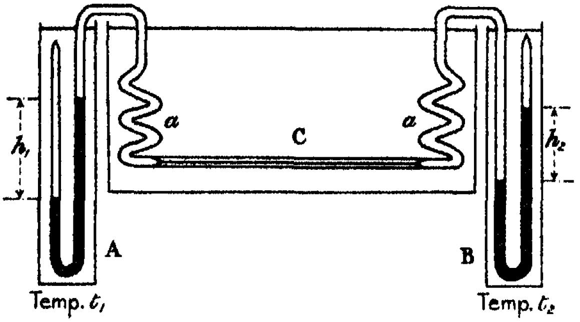

FIG. 2.

there; consequently the saturation pressures are maintained. In the limbs adjacent to the capillary, however, owing to rapid evaporation and condensation, the pressures differ from the saturation values, but by amounts which can be easily estimated by observing the differences of level in the two limbs of the U-tubes. Thus suppose t_1 and t_2 are the temperatures of the baths containing A and B respectively, ρ_1 and ρ_2 the densities of the liquid at these temperatures, p_1 and p_2 the pressures at the two ends of the capillary, and h_1 and h_2 the differences of levels of the liquid in the respective U-tubes, then

$$p_1 = (\text{saturation pressure at } t_1) - g\rho_1 h_1,$$

$$p_2 = (\text{saturation pressure at } t_2) + g\rho_2 h_2.$$

Thus, provided that the saturation vapour pressures and the liquid densities over a small temperature range are known, the pressures controlling the transpiration can be found without using anything in the nature of an ordinary pressure gauge. Further, a knowledge of the specific volumes of vapour and liquid provides means of determining the rate of flow through the capillary, from observations of the volume evaporation and condensation of the liquid.

Although the results recorded here are confined to bromine, the method will probably be found suitable for measuring the viscosity of the vapours of such elements as iodine, phosphorus, and sulphur, besides many volatile organic substances.

Experimental Details and Dimensions of Apparatus.

It happens that, in the case of bromine, a suitable pressure difference may be secured by keeping one of the U-tubes at the temperature of melting ice, and the other slightly below atmospheric temperature. They were therefore enclosed in deep rectangular vessels with plate glass sides, which could be filled either with a mixture of crushed ice and water or water near the temperature of the atmosphere. Both were kept thoroughly stirred by means of paddles, and by this means fairly constant temperatures were maintained. The low-temperature side remained steadily a few hundredths of a degree above 0° C., while the other side warmed so slowly—at most about ½° C. per hour—that it was quite justifiable to take the mean value as the effective temperature. The capillary tube and spirals were in a large copper vessel which contained water for the lower temperatures and liquid paraffin for temperatures above 100° C. By reason of the large amount of liquid present, which was kept thoroughly stirred throughout, the temperature could easily be kept practically constant by suitably adjusting the gas supply. The vessels A and B (fig. 2) were effectively shielded from C. Observations were obtained with C at six different temperatures ranging from 13° C. to 220° C. The rate of evaporation of liquid was naturally diminished by raising the temperature of the capillary, both on account of the increase of specific volume of the vapour and its increased viscosity. The adjustment was, however, not wholly effected in this manner, and it was rather surprising to find that the rate of evaporation was not greatly diminished. The explanation lies in the fact that the pressure difference between the ends of the capillary assumed a higher value; in other words, the experiment approached more nearly to the ideal case referred to in the beginning of this paper.

The U-tubes A and B were about 2 mm. in internal diameter, and each limb was about 20 cm. long. They were graduated in millimetres and carefully calibrated. The length of the capillary tube was about 39 cm., and the radius approximately 0·018 cm. In transpiration experiments, however, the dimension required is the effective value of l/R^4, where l is the length and R the radius of the equivalent uniform capillary. In order to allow for the conical ends and other irregularities in the tube, calibration with a short thread of mercury was used in order to determine the sum $\Sigma(\delta l/r^4)$, where δl is any short length and r the radius in that neighbourhood. The advantage of this method is that it gives proper weight to the retarding effects of the various portions of the tube, and indicates how far it is justifiable to ignore the viscous retardation in parts of the apparatus other than the capillary

itself. In the apparatus in question no correction comparable with the experimental error was necessary on this account. The actual value of $\Sigma(\delta l/r^4)$ was $3{\cdot}763 \times 10^8$ cm.$^{-3}$.

The method of obtaining the data necessary for calculating the rate of flow of gas and the pressures at the two ends of the capillary was to take time readings of the positions of the four liquid levels—two on the evaporation side and two on the condensation side. The masses of bromine evaporating and condensing in the same given time were always found to be nearly equal, but calculations have been made from the rate of evaporation only, since there was no guarantee that the whole of the condensed vapour found its way at once into the liquid already there; in other words, the amount of liquid in the process of flowing down the walls of the condensation tube at any given instant was not necessarily constant. The readings on the condensation side were, however, necessary for the estimation of the pressure, and the average difference of level both on this side and on the evaporation side throughout an experiment were found in each case. An experiment usually lasted rather more than an hour, 12 or 14 observations of each level being taken in this time. The temperatures both in the baths A and B and in the tank C (fig. 2) were obtained by means of thermometers specially standardised for the purpose, the probable accuracy being 0·01° C. in the case of A and B, and an amount varying from 0·1° C. to 0·5° C. according to the temperature in the case of C.

The apparatus was entirely devoid of taps both in its final form and during the process of filling, absence of tap grease being regarded as necessary in order to avoid the production of impurities due to chemical action upon it by the bromine.

The bromine used was of the purest quality supplied by Kahlbaum. Some difficulty was experienced in securing that the contents of the apparatus consisted only of the liquid and its vapour. Eventually the following method of procedure was adopted with success. The apparatus was first of all evacuated as far as possible by means of a mercury pump, the latter then being sealed off, leaving charcoal tubes which could be placed in liquid air to remove final traces of permanent gas. The liquid bromine was then introduced by breaking off the end of a narrow tube placed below its surface. When a sufficient quantity had entered, the narrow tube was sealed off. With the charcoal tubes now in liquid air, a portion of the bromine was allowed to evaporate so as to rid it of gases which might be dissolved in it, and finally the charcoal tubes were sealed off, and the liquid distilled into the U-tube A. It was noticed that, even after this procedure, a small quantity of permanent gas had survived; indeed circumstances at this stage seemed to

indicate that the bromine vapour exercised a displacing action upon other gases condensed in the charcoal, and it was only by making use of a series of separate charcoal tubes that the impurity was reduced to an amount which would not seriously affect the measurement. Although a small admixture of foreign gas would not greatly alter the viscosity, it was important to remove any trace of it from the closed limbs of the U-tubes, otherwise the pressures at these points would not have the estimated values, namely, the saturation pressures of the bromine. This was done by successive condensation and evaporation of the bromine in the U-tubes, and that the process had been successful was evident from the fact that afterwards, if the closed limbs were cooled, they would become completely filled with liquid.

Calculation of Results.

Meyer's transpiration formula, upon which the present method of measurement is based, is

$$\eta = \frac{\pi R^4}{16 l} \cdot \frac{(p_1^2 - p_2^2)t}{p_1 v_1},$$

where η is the viscosity, R the radius and l the length of the capillary tube, t the time during which a volume v_1 enters the tube, and p_1 and p_2 the respective pressures at the ends where inflow and outflow occur.

This formula is developed upon the assumption that the gas in question obeys Boyle's law. It is quite possible, therefore, that if we are dealing with a gas which is only slightly superheated, we may not be justified in using this means of finding the viscosity. Indeed, this very fact may be the cause of certain irregularities which are observed in the case where the temperature of the capillary tube is only a few degrees above that of the evaporating bromine. For lack of precise information on this question, however, there was nothing to be done but to assume the validity of the formula in all cases. The same objection possibly applies also to the assumption that Charles' law is true for the vapour in the rarefied condition in which it was used, as has been done in order to connect the volume of liquid evaporating with that of the gas entering the capillary. Both these points will be treated more fully later in the paper.

With the above assumptions we may write in the transpiration formula

$$\frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0},$$

where T_1 = the absolute temperature of the capillary, p_0 and T_0 being normal pressure and temperature, and v_0 the volume of gas reduced to N.T.P.

Further $$m = \rho_0 v_0,$$

where m is mass of gas traversing the capillary and ρ_0 its density at N.T.P.

Meyer's formula therefore becomes

$$\eta = \frac{\pi R^4}{16l} \cdot \frac{(p_1^2 - p_2^2)t}{p_0 m} \cdot \rho_0 \frac{T_0}{T_1},$$

the quantities variable from one experiment to another being p_1, p_2, m, t, and T_1.

The density of bromine at N.T.P., *i.e.* ρ_0, was estimated from the value of the atomic weight, 79·96, relative to oxygen. The value obtained and used was 0·007161 grm. per cm.^{3}. As has been shown, the vapour pressure of bromine and the density of the liquid over a temperature range from 0° C. to about 16° C. were needed in order to calculate p_1 and p_2 from the experimental observations. The densities were also necessary to obtain m in terms of the volume of liquid evaporating.

For the former purpose the vapour pressures due to Ramsay and Young* were taken, and to their observations was fitted, by the method of least squares, over the small necessary temperature range a parabolic formula, so as to be able to interpolate. The values of the densities of liquid bromine at various temperatures were taken from the mutually consistent results of Pierre,† Quincke,‡ J. D. van der Plaats,§ and Andrews and Carlton.‖ They range from 3·187 grm. cm.$^{-3}$ at 0° C. to 3·102 grm. cm.$^{-3}$ at 25° C.

Small corrections were also applied for the expansion of the capillary tube with temperature and for the slipping of the gas over its internal walls. The former correction amounted to about 0·5 per cent. at the highest temperature at which observations were taken; the latter, which would have been almost negligible had the gas been at atmospheric pressure, was comparatively important by reason of the fact that the average pressure in the experiments was of the order of 10 cm. of mercury only. The correction for slipping, as is well known, amounts to multiplying the original Meyer's expression by the factor $(1+4\lambda/R)$, R being the radius of the capillary and λ a quantity which differs little from the mean free path of the gas molecules under the conditions of the experiments. The value of λ needs to be known only approximately for correction purposes, and in the present cases a sufficiently accurate value was obtained by adopting the method used by the author in previous determinations,¶ namely, to calculate λ from the approximate value of the viscosity, using the customary formula based on the kinetic theory.

* Ramsay and Young, 'Chem. Soc. Journ.,' 1886, vol. 49, p. 453.

† Pierre, 1848.
‡ Quincke, 1868.
§ J. D. van der Plaats, 1886.
‖ Andrews and Carlton, 1907.
These values were obtained from Landolt and Börnstein's tables.

¶ 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 517.

More accurate values of λ can, if required, be subsequently obtained by the method of repeated substitution. Owing to the rarefied condition of the gas in the present measurements, λ had considerably greater values than under normal circumstances, consequently the corrections on account of slipping were correspondingly greater, amounting to from 0·5 to 2 per cent., according to the temperature.

Although evidence will be given later to show that very probably bromine vapour obeys Maxwell's law, viz., that the viscosity of a gas is, over a large range, independent of the pressure, it has been thought desirable to record the values of p_1 and p_2 and their mean value. These are given (in centimetres of mercury) in Columns 2, 3, and 4 of Table I, where the results of all the experiments are tabulated. The rates of transpiration, *i.e.* the number of grammes of vapour traversing the capillary per second, are also given in Column 5. It may be mentioned, in this connection, that calculations were made to see whether an appreciable reduction in driving pressure was brought about by the velocity of transpiration of the vapour, but the amount was found to be much below the probable accuracy of the measurements.

Table I.

Temperature (absolute).	p_1.	p_2.	Mean pressure.	Transpiration rate in gr.-sec.$^{-1}$ × 10^4.	Viscosity in C.G.S. units × 10^4.
285	9·17	7·70	8·44	1·041	1·509
284·6	9·57	7·59	8·58	1·425	1·508
286·8	10·25	7·58	8·92	1·957	1·525
287·1	9·15	7·57	8·36	1·108	1·504
338·7	10·48	7·50	8·99	1·669	1·718
339	10·42	7·57	9·00	1·592	1·707
338·6	10·52	7·52	9·02	1·706	1·691
372·8	10·12	7·55	8·84	1·181	1·868
372·9	10·35	7·57	8·96	1·284	1·888
372·6	10·58	7·53	9·06	1·418	1·898
413·7	12·05	7·73	9·89	1·802	2·086
413	11·32	7·74	9·53	1·448	2·066
412·8	11·65	7·73	9·69	1·597	2·086
452·8	11·18	7·97	9·58	1·099	2·247
452·7	11·35	8·06	9·70	1·124	2·280
452·9	11·48	8·01	9·75	1·186	2·293
493·5	11·81	8·34	10·07	1·045	2·468
493·3	12·54	8·31	10·42	1·307	2·492

It will be noticed that, in each of the groups indicated above, the temperatures are approximately the same, and that the variations in values of the

viscosity in any group amount to about 1 per cent. This, indeed, represents very nearly the degree of accuracy which could be expected from the particular form of apparatus used.

In Table II there are collected the mean values deduced from the previous table, and the same data are shown graphically in fig. 3.

Table II.

Temperature (absolute).	Viscosity in C.G.S. units × 10^4.
285·9	1·511
338·8	1·705
372·8	1·885
412·8	2·079
452·8	2·273
493·4	2·480

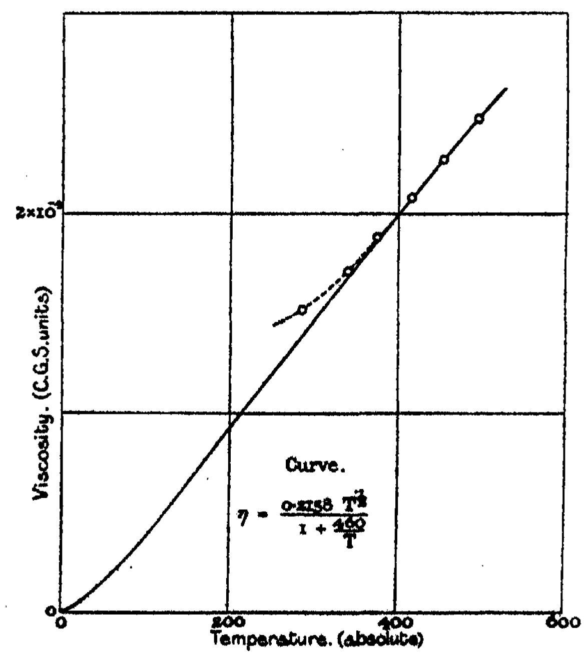

Fig. 3.

In view of the number of separate observations taken at the various temperatures, the probable error is considerably less than 1 per cent.

Discussion of Results.

There are several points of interest in connection with the results which have been obtained. In the first place, it is possible to compare one of

the present determinations with a corresponding determination previously obtained by the author by a different method.* In that case the viscosity of bromine vapour was measured at 98·7° C. and atmospheric pressure. The value obtained was $1{\cdot}869 \times 10^{-4}$ C.G.S. units, and in the present case, at a pressure of about 9 cm. of mercury and a temperature of 372·8° abs., *i.e.* 99·8° C., the viscosity is found to be $1{\cdot}885 \times 10^{-4}$ C.G.S. If we interpolate so as to make the temperatures of the two values under comparison identical, the result obtained is $1{\cdot}879 \times 10^{-4}$ at 98·7° C. This is only about $\frac{1}{2}$ per cent. different from the value measured by means of the earlier and entirely different apparatus and method. It seems justifiable, therefore, to conclude that the viscosity of this vapour is independent of the pressure, at any rate, through the range from 9 to 76 cm. of mercury, notwithstanding the fact that it may be only comparatively slightly superheated. It is worthy of notice also that the accordance of these two results suggests that within the degree of accuracy attained in these viscosity measurements it is probable that Boyle's law is valid, and its use in the calculation of these results permissible, at and above the temperature in question.

When we come to consider the mode of variation of the viscosity with temperature, we are met with the, at first sight, surprising result that the viscosity increases more and more rapidly as the temperature rises (fig. 3). The experimental points lie on a curve which is at first concave upwards and becomes practically straight at the higher temperatures. As far as the author is aware, no previous viscosity determinations with any gas have indicated this type of variation with temperature. No gas even approximately obeys the law deduced from the simple kinetic theory over the temperature range which has up to the present been treated experimentally; but the departures from this law hitherto observed have not been sufficiently great to alter the sign of the curvature of the theoretical curve. Ultimately, no doubt, at exceedingly high temperatures the viscosity of every gas would be proportional to the square root of the absolute temperature, but the present measurements show that at comparatively low temperatures the departures from this law are great enough to produce an actual inflexion in the curve connecting viscosity with temperature. In this connection it is interesting to observe that the equation which Sutherland proposed does show such an inflexion. The curvature of his curve $\eta = \kappa T^{\frac{1}{2}}/(1+C/T)$ (κ and C being constants) changes sign at $T = (2\sqrt{3}-3)\,C$ or 0·464 C. This has, the author believes, not been called attention to previously, probably because no such variation has been found experimentally. For nitrogen, for

* 'Roy. Soc. Proc.,' 1912 A, vol. 86, p. 166.

instance, the value of C which has been found is 113, and assuming Sutherland's equation to be valid at such temperatures, measurements of the viscosity at 52° absolute would be necessary to reach the point of inflexion, and at still lower temperatures to indicate the upward curvature. In this region the nitrogen would be normally liquid; indeed, speaking generally, all gases are so at the absolute temperature $0·464 \times C$, so that from this point of view experiments with the vapour at low pressures would be required to indicate this type of variation.

This is, in fact, what has been done in the present case, and although it turns out, upon closer consideration, that the correspondence, from other standpoints, between the experimental results for bromine and Sutherland's equation is by no means close, yet the very fact that the inflexion of the curve appears both practically and theoretically seems to favour the view that the modifications of the simple kinetic theory introduced by Sutherland are upon the right lines. However, the attempt to fit Sutherland's equation to the experimental points as they stand is unsuccessful. The equation involves that at absolute zero the slope of the curve is zero, and a reference to fig. 3 will show that the positions of the points are not such that a continuation of the curve through them would satisfy this condition. If, however, the two lowest temperatures are omitted from the calculation, very good agreement with Sutherland's equation is shown by the remaining four. The full curve in fig. 3 represents the equation fitted to the upper four points, and it has been continued down to absolute zero, both to show the divergence for the lower points and the point of inflexion previously referred to. In the following table (Table III) are given the observed values of the viscosity and the values calculated according to the equation

$$\eta = \frac{0·2158\,T^{\frac{1}{2}}}{1+460/T} \times 10^{-4}.$$

Table III.

Temperature (absolute).	Viscosity × 10^4.		Difference, per cent.
	Observed.	Calculated.	
493·4	2·480	2·481	−0·0
452·8	2·273	2·278	−0·2
412·8	2·079	2·074	+0·2
372·8	1·885	1·866	+1·0
338·8	1·705	1·685	+1·2
285·9	1·511	1·399	+6·2

There is obviously more probability that the equation of Sutherland will approximate more closely to the facts at higher than at lower temperature. Indeed he made no claim that it would be valid where the gas was only slightly superheated. The changes necessary to be made in the gas theory must apparently be such as will retain and at the same time raise the point of inflexion.

An alternative explanation of the divergence from the theoretical curve of the lowest point in particular is that in the observations upon which this value is based the vapour was so slightly superheated (a few degrees only), and that consequently it could not be treated as a perfect gas in the calculation of the viscosity. It seems unlikely, however, considering the fact that the pressure was so low, that an error so large as 6 per cent. would be introduced on this account.

One other point, perhaps, also deserves mention. No data are available to show what degree (if any) of association exists in the bromine vapour under the circumstances of the experiments. Obviously this might have an important effect, particularly if, as is almost certain, dissociation occurred with rise in temperature. The agreement between the values at 98·7° C., but at considerably different pressures, previously referred to is distinctly against the occurrence of appreciable association, at any rate, at that temperature.

These considerations only apply to the lower temperatures, and we may take it that at the higher temperatures Sutherland's law fits in with the facts to a considerable degree of accuracy. It is possible, therefore, to test the agreement or otherwise of the data presented in this paper with the two laws in connection with gaseous viscosities which the author has previously shown to apply in other cases.*

The first of these is that, for a large number of gases, Sutherland's constant C is proportional to the critical temperature, the relation being expressed by the equation

$$T_c/C = 1 \cdot 14.$$

The critical temperature of bromine, according to Nadejdine, is 575° absolute, and the above ratio has the value $575/460 = 1 \cdot 25$. This ratio is distinctly higher than 1·14, and in this respect bromine is similar to chlorine, the ratio for which is 1·28.† It appears, therefore, that although various gases without distinction of kind obey this law approximately, still better agreement is obtained when the application is confined to a single group in the periodic system.

* 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 190; 'Phil. Mag.,' January, 1911, p. 47.

† 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 166.

The second law may be stated as follows :—For the group of inert gases the square of the viscosity at the critical temperature is proportional to the atomic weight, or

$$\eta_c^2/A = \text{constant} = 3{\cdot}93 \times 10^{-10}.$$

In this numerical value η_c is in C.G.S. units and A is the atomic weight relative to oxygen. It should be pointed out that η_c is not the viscosity in the critical state, but merely the viscosity at the critical temperature, when the pressure has such values that the viscosity is independent of it. Using the values of the viscosity of bromine given in this paper, and those for chlorine communicated in a previous paper, it is possible without violent extrapolation (some 47° C. in the case of chlorine, and 82° C. in the case of bromine) to obtain by means of Sutherland's equation the viscosities at the critical temperatures.

These values are based upon Knietsch's determination (419° abs.) for the critical temperature of chlorine, and Nadejdine's determination (575° abs.) for bromine. Applying these estimates to the test under consideration the results are as follows :—

Table IV.

Gas.	Viscosity at critical temperature. η_c (C.G.S. units).	η_c^2/A.
Chlorine	$1{\cdot}897 \times 10^{-4}$	$1{\cdot}02 \times 10^{-9}$
Bromine	$2{\cdot}874 \times 10^{-4}$	$1{\cdot}03 \times 10^{-9}$

It will be at once seen that the numbers in the last column are practically identical, although not at all the same number as that for the inert gases. This suggests the possibility of the law in question being of wider application than merely to the inert gases, with the restriction that the constant of proportion is not universal, but has values peculiar to each group in the periodic table.

Finally, the values of the viscosity have been used to estimate the molecular dimensions of the two gases. For this purpose the number of molecules per cubic centimetre at N.T.P. has been taken as $2{\cdot}75 \times 10^{19}$, and Sutherland's correction arising from the intermolecular attractions has been applied. The molecular diameters and volumes are both recorded in Table V.

Table V.

Gas.	Molecular diameter (in cm. $\times 10^8$).	Molecular volume (in cm.$^3 \times 10^{22}$).
Chlorine	3·15	1·30
Bromine	3·36	1·59

Apparently the dimensions of the molecules do not differ to any great extent, and this, of course, involves that the density of the atom of bromine is something like twice as great as that of chlorine.

The Hall Effect in Liquid Electrolytes.

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(Communicated by Sir J. J. Thomson, O.M., F.R.S. Received May 8,—Read June 19, 1913.)

Introduction.

The distortion of the lines of flow of an electric current in a thin metal plate by the action of a magnetic field was discovered in 1879.* Hall attributed this to the action of the magnetic field on the molecular currents in the metal film, which were deflected to one side or the other and accompanied by a corresponding twist of the equipotential lines. This explanation did not pass without criticism, and another theory of the effect found by Hall was published in 1884.† In that paper the author seeks to explain the effect by assuming a combination of certain mechanical strains and Peltier effects, a thermo-electric current being set up between the strained and the unstrained portions. The effect of such strain was to produce a reverse effect in some metals, and these were precisely the metals for which the Hall effect was found to reverse. Aluminium was the only exception.‡

In other respects, however, as shown by Hall in a later paper,§ Bidwell's

* E. H. Hall, 'Amer. Journ. Math.,' vol. 2, p. 287; 'Phil. Mag.,' 1880, vol. 9, p. 225.

† S. Bidwell, 'Roy. Soc. Proc.,' 1884, vol. 36, p. 341.

‡ 'Nature,' vol. 29, p. 514; 'Chem. News,' vol. 49, p. 147.

§ 'Science,' vol. 3, p. 387; 'Phil. Mag.,' 1885, vol. 19, p. 419.

theory did not stand the test of experiment, and the results lend no support to his theory, while they are in complete accordance with the explanation that the molecular currents are disturbed by the action of the magnetic field. On the electron theory of metallic conduction, the mechanism of the Hall effect is more obvious, but at present no satisfactory explanation of the reversal found in some metals is known. Further experiments have made it clear that there is a real deflection of the elementary currents, due to the application of the magnetic field, independent of any effect due to strain.

The first attempt to measure the Hall effect in gases was made by Marx in 1900.* The velocities of the ions from flames are about one million times the ionic velocities in liquids, and, what is very important, there is in this case a considerable difference between the velocities of the two kinds of ions. Marx succeeded in showing that a small though appreciable Hall effect existed in such flame gases and verified completely the predictions of the convective theory.

In 1902, H. A. Wilson† showed that the Hall effect was large in the positive column of the discharge tube, at low pressures, the effect being proportional to the intensity of the magnetic field.

There are certain considerations which lead us to suppose that a true Hall effect exists in liquid conductors. In the first place, a liquid conductor contains ions which, owing to their motion, constitute elementary molecular currents. In the second place, it has been established that the presence of strains is not an essential factor in the production of the effects sought. Although the effect will necessarily be small, on account of the low value of the mobility of the ions in electrolytes, still there is every reason to suppose that it does exist and that the difficulty lies in our not being able to appreciate the small effects, which are likely to be masked by disturbing forces.

Review of Past Work on Liquids.

Roiti,‡ in 1882, attempted to observe the Hall effect in a thin liquid lamina, the liquid being enclosed between two plates of glass (55 mm. × 60 mm.) separated by a distance of 0·05 mm. The results obtained were complex and difficult to interpret. Roiti holds the opinion that they are due to local variations of concentration.

In 1896 Roiti's research was repeated by Bagard,§ who claimed to establish

* 'Ann. der Phys.,' 1900, vol. 2, p. 798.

† 'Proc. Camb. Phil. Soc.,' 1902, vol. 11, p. 249.

‡ 'Atti R. Accad. Lincei,' 1882, vol. 12, p. 397.

§ 'Comptes Rendus,' 1896, vol. 122, p. 77; 1896, vol. 123, p. 1270.

the existence of the Hall effect to a high degree in liquids. In Bagard's experiment the liquid layer was horizontal and the bounding plates were 53 mm. × 30 mm., the distance between the plates being 1·6 mm. A water bath was used to prevent disturbances due to temperature variations. The pole pieces of the electromagnet had square plates (5 cm. side) attached to them, and the plates were separated by a distance of 2·5 cm. Bagard considered that the field was uniform in the central region of the lamina.

Here it is important to consult a research by Voigt* concerned with the alteration of the concentration of a salt solution placed in a non-uniform magnetic field. The effect of such variations of concentration, even if they occur at the boundary of the lamina only, will be sufficient, in a short time, to produce diffusion of the salt from the central region. This may give rise to a potential difference which is considerably greater than the estimated value of the Hall effect. As Roiti had found, the effect was not produced instantaneously; the rate of growth was large at first and small afterwards and varied with the concentration of the solution. Both Bagard and Roiti used a capillary electrometer to measure the transverse potential difference.

Shortly afterwards, Bagard's research was repeated by Florio,† under precisely the same conditions. He obtained a negative result, and attributed the large effects found by Bagard partly to disintegration of the electrodes and partly to disturbances produced by vibrations. The dimensions of the lamina used by Florio were 11 cm. × 10 cm. × 1·6 mm., and the pole pieces had a diameter of 13 cm.

The experiments of Bagard have been further tested by Chiavassa,‡ who took every precaution to reproduce the original conditions as accurately as possible. He concluded that the effect observed by Bagard was spurious and due to variations of temperature and of concentration, the latter being caused by non-uniformity of the magnetic field over the region occupied by the lamina. Chiavassa found that a small liquid film exposed to a uniform magnetic field gave no indication of a Hall effect. A capillary electrometer, which would detect 0·00005 volt, was used to measure the transverse potential difference.

Two more attempts have been made to discover the existence of the Hall effect in liquids. These were made in 1904 by Heilbrun§ and in 1908 by Delvalez.‖ Heilbrun used a triple cathode and investigated the redistribution

* 'Gött. Nach.,' 1910, p. 545.

† 'Nuovo Cimento,' 1896, vol. 4, p. 106; 1897, vol. 6, p. 108.

‡ 'Nuovo Cimento,' 1897, vol. 6, p. 296.

§ 'Ann. der Phys.,' 1904, vol. 15, p. 988.

‖ 'Journ. de Phys.,' 1909, vol. 8, p. 360.

of the deposit on each portion under the action of a magnetic field. The small variations observed were attributed to movements of the electrolyte. Delvalez used an alternating primary current and a telephone as indicator in the transverse circuit. He showed that the Hall coefficient, if it exists, does not exceed the value 5×10^{-9}, a magnitude nearly ten thousand times greater than that which theory indicates.*

The question of the existence of a true Hall effect in liquid electrolytes is therefore an open one. It seems probable, however, that such an effect exists, and that it is because the methods hitherto adopted to detect it have not been delicate enough that no satisfactory confirmation of the theory has been made.

Mr. H. L. P. Jolly, of Trinity College, placed his galvanometer, designed by Prof. Paschen, at my disposal, and I resolved to make an attempt to detect the effect indicated by theory. With the aid of such a delicate instrument it was hoped at least that the upper limit of the value of the Hall coefficient, 5×10^{-9}, obtained by Delvalez, would be considerably reduced.

The value of the expected effect will now be considered. If the potential gradient of the Hall effect along the z axis be denoted by $\partial e/\partial z$, and the potential gradient between the primary electrodes by $\partial \pi/\partial x$, then Donnan has shown that

$$\frac{\partial e}{\partial z} = \frac{\omega \epsilon}{L+M}(Lv - Mu)H\frac{\partial \pi}{\partial x}, \tag{1}$$

where H is the strength of the magnetic field, u and v are the velocities acquired under unit force by 1 grm.-mol. of positive and negative ionic matter, ω is the valency of each ion and ϵ is the quantity of electricity per gramme-equivalent of ionic matter. L and M are two factors depending for a partially dissociated electrolyte on the equilibrium equation

$$C = \phi(c),$$

and are connected with the concentration of the dissociated salt c and of the undissociated salt C, by the relations

$$L = \frac{2G\phi'(c)}{u} + 1,\dagger \qquad M = \frac{2G\phi'(c)}{v} + 1.$$

Writing $\omega\epsilon u = U$ and $\omega\epsilon v = V$, where U and V are the velocities acquired by a gramme-molecule of positive or negative ionic matter under unit potential gradient, the coefficient of the Hall effect is

$$\frac{\partial e/\partial z}{H\,\partial\pi/\partial x} = \frac{LV - MU}{L+M}.$$

* Donnan, 'Phil. Mag.,' 1898, vol. 46, p. 465; Larmor, 'Æther and Matter,' p. 301; van Everdingen, 'K. Akad. v. Wetensch. Amsterdam,' vol. 1, p. 27.

† G is the velocity acquired by 1 grm.-mol. of undissociated salt when acted on by unit force.

Donnan shows that the value of the Hall coefficient, assuming that the electrolyte is completely dissociated ($L = M = 1$) is

$$\tfrac{1}{2}(V-U) = 16 \times 10^{-13},$$

and the transverse potential difference due to it will be

$$e = 16 \times 10^{-13} Hz$$

for a fall of 1 volt per centimetre between the primary electrodes.

If $H = 15{,}000$ gauss and $z = 1$ cm., then

$$e = 2{\cdot}4 \times 10^{-8} \text{ volt.}$$

Superposed on this effect is the difference of potential due to change of ionic concentration* and this is shown by Donnan to have the value

$$e' = \tfrac{1}{2} H (U+V) z \frac{\partial \pi}{\partial x}. \tag{2}$$

Taking $z = 1$ cm., and $\partial\pi/\partial x = 1$ volt per centimetre, we have, for a field of 15,000 gauss,

$$e' = 0{\cdot}9 \times 10^{-7} \text{ volt,}$$

for a completely dissociated electrolyte. e' is larger than e. Nevertheless this potential difference, if it can be measured, will be as true an indication of the existence of a Hall effect as the potential difference e is. Further, on the above theory, the existence of e' implies that of e.

In the experiments described later it was found difficult to make observations within 15 seconds from the moment of exciting the magnetic field, so that probably the resultant of the two effects was observed.

It is impossible to measure the initial Hall effect, which is twice as large as the stationary Hall effect, because the stationary state has been reached by the time an observation is taken.

The effect arising from (1) will, in what follows, be referred to as the true Hall effect, while that arising from (2) will be called the concentration Hall effect.

Description of Apparatus and Method.

Fig. 1 is a diagram showing the arrangement of the apparatus. M, M are the pole pieces of the electromagnet and L is the liquid lamina placed between them. The primary circuit through the cell containing the liquid lamina is completed by the resistance R and the primary current is supplied by the battery B_1.

The electromagnet circuit contained three rheostats R_1, R_2, R_3, a reversing key K, and a Siemens-Halske ammeter A. A battery of 20 large cells supplied the current.

* *Vide* Donnan, *loc. cit.*, p. 466.

G represents the Paschen galvanometer. C is a control magnet fixed vertically above the galvanometer so that the sensitiveness could be varied by raising or lowering it, while the zero could be adjusted by turning it round. The distance from the electromagnet to the galvanometer was

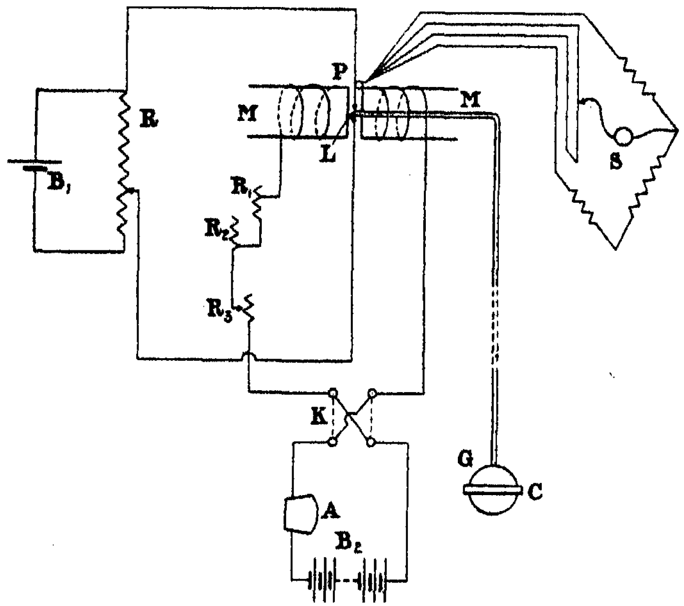

FIG. 1.

25 metres. At this distance the effect of the permanent field when the magnet was excited was small and varied from one experiment to another, depending upon the distance between the pole pieces and the intensity of the exciting current. Throughout an experiment this small change of zero remained of constant amount.

This form of galvanometer possesses advantages over the Broca galvanometer in that its period of swing for maximum sensitiveness is 7·5 secs. only, as compared with 17·3 secs., while its normal sensitiveness is 10 times that of the Broca galvanometer. The galvanometer was mounted on a stone slab supported by pillars which are built into the foundation of the Cavendish Laboratory. But during the day time the galvanometer zero was unsteady and therefore the observations were made at night. On one evening only were slight erratic disturbances noted, otherwise the zero was very steady.

The suspended system of the galvanometer consists of a fine glass rod about 8 cm. long, to the centre of which is attached a plane rectangular

mirror M (fig. 2). The system was made almost perfectly astatic by two groups of magnets M_1 and M_2, each consisting of 15 small magnets fixed to the glass rod. The system was suspended by a fine quartz fibre, so that M_1 and M_2 each filled an oval-shaped cavity formed by a pair of coils. When all the four coils are connected in series, as in the present experiments, the resistance of the galvanometer is 16 ohms.

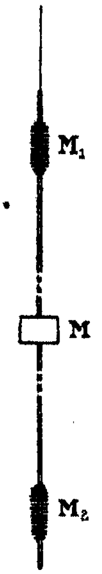

FIG. 2.

The Cells.—(a) *For Liquids:* The outside dimensions of the cell are 19 × 19 × 1·4 mm. To construct one, a micro-square was taken and four small blocks of ebonite, cut from the same ring and approximately 1 mm. thick, were fixed at the four corners by specks of Canada balsam. A second micro-square was cemented to the tops of these, and three sides of the skeleton so formed were sealed with beeswax and resin. In fig. 3, *b*, *b*, *b*, *b*, are the ebonite blocks, P_1, P_2, the primary electrodes of pure copper wire, and T_1, T_2, the transverse electrodes of fine pure copper wire. The upper transverse electrode was movable and capable of fine adjustment.

(b) *For Copper Sulphate Gel:* A copper sulphate gel was prepared, placed upon the table of a microtome and frozen with ether. Thin sections of the gel were cut, thrown into water for a few moments, withdrawn and mounted on sheets of mica. The edges of the gelatine film were trimmed so as to form a square of about 2 cm. side. Fig. 4 is a diagram of the cell. The adjustment of the transverse electrodes

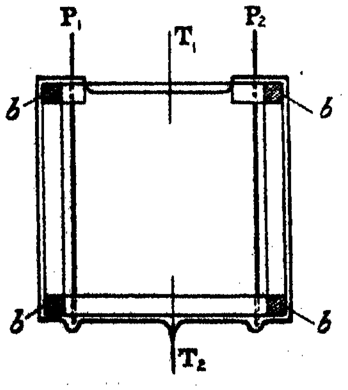

FIG. 3.

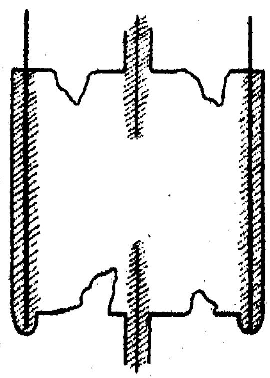
FIG. 4.

to the same equipotential was made by scraping away the gelatine. In order to secure good contact of the electrodes with the gel, the electrodes were laid in position on the microtome section and a layer of warm gel was

painted over them. The positions of the thicker layers of gelatine are shown by the shaded areas of the figure.

The type (*a*) of cell was mounted on a rigid brass support A (fig. 5), which was fixed to a heavy lead block B. The latter rested on a slate bed C, which had square rails screwed to it, and on these rails slid a brass carrier N, whose position could be adjusted by a screw motion. The movable electrode was attached to the glass rod S, and adjustments corresponding

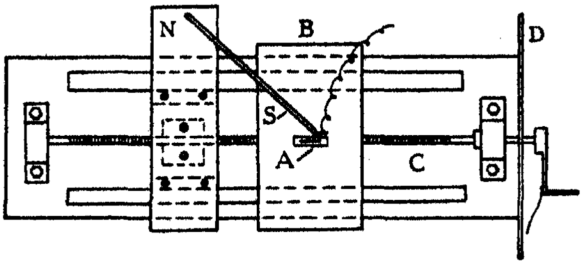

Fig. 5.

to 1/1800 of the applied primary potential gradient could be made by moving the pointer over one division of the scale D.

A Grassot fluxmeter was employed to measure the intensity of the magnetic field and, with the search coil used, the full scale deflection corresponded to 22,300 gauss. The creep of the pole pieces was prevented by a wedge of brass.

To ensure that the temperature in the neighbourhood of the cell remained constant during an experiment, a small platinum thermometer was inserted just inside the gap. This thermometer was provided with compensating leads, and the temperature measured as shown at S (fig. 1).

A very small primary voltage was applied to the cell and the movable electrode adjusted or the equipotential lines twisted until the galvanometer gave a small deflection only. The primary potential gradient was now increased, and the same operations repeated until a voltage was reached beyond which the galvanometer zero was unsteady owing to irregularities in the action of the cell. The constancy of the zero was tested carefully in each case. The galvanometer circuit was now opened for a few seconds until induction effects due to the application of the magnetic field had died away, and the new zero of the galvanometer due to the presence of the magnetic field was noted. Several deflections were taken, each about 10 seconds after closing the galvanometer circuit. A similar series of observations was taken with the magnetic field reversed.

The importance of a uniform magnetic field cannot be overstated, for

minute motions of the electrolyte give rise to relatively large potential differences. Accordingly the cells were made much smaller than those which have been used hitherto, the area being about 4 sq. cm., whilst that of the pole pieces was 50 sq. cm. In all the researches referred to in the review of past work, the cells were of dimensions comparable with the size of the pole pieces. Further, in the present experiments the air gap was reduced as much as possible, not so much for the reason of creating a large magnetic field, although that is desirable, as for procuring a uniform field over the whole region occupied by the cell. Rarely were the pole pieces closer than 1 cm. in the experiments which have hitherto been made, and in some experiments they were as much as 2·5 or 3·0 cm. apart. In such cases it is most improbable that the magnetic field is uniform in the neighbourhood of the boundary of the cell, when a large cell is used, and consequently the salt begins to move up or down the gradient of the magnetic field according as it is paramagnetic or diamagnetic. This will give rise to motions of the fluid in the central part of the cell.

Chiavassa has shown that if we take a small cell and ensure that the magnetic field is uniform, then the effects found by the earlier experimenters entirely disappear. It is with the object of pursuing this question with a more delicate means of measuring the transverse effect that the present research was carried through. Differences of concentration throughout the cell are of secondary importance if the field is very uniform and so long as these differences remain constant. This is true, for instance, in a cell used vertically, as in the present experiments, where, through the action of gravity, the lower layer is more dense than the upper one.

To avoid disturbances due to air currents the cell was surrounded with pads of cotton wool and the junctions in the galvanometer circuit enclosed in glass tubes. The solutions were transferred to the cell by means of a capillary tube, and the presence of air bubbles thereby prevented. A syphon was provided in the later experiments to keep the cell full.

Experiments.

Copper Sulphate Solution.—An estimation by the iodine method was made and the solution was found to contain 13·3 grm. of copper sulphate per litre.

In the following table z_1 is the zero position on the scale when the galvanometer circuit is open, z_2 is the deflected position when the circuit is closed and the primary current is flowing, z_3 is the deflected position when, in addition, the magnetic field H is applied.

A preliminary experiment was made on March 15, 1912, the observations being taken to the nearest scale division only.

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
7·0	6·0		−1·0		+1·0	0
7·0		7·0		0·0		+9900

March 16, 1912.—Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
19·0	18·0		−1·0		+1·0	0
19·0		19·0		0·0		+9900

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
20·0	22·5		+2·5		−1·5	0
20·0		21·0		+1·0		−9900

March 18, 1912.—The cell was washed out with copper sulphate solution and refilled. The following readings were taken :—

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
20·3	25·3		+5·0			0
*19·9		24·4		+4·5	−0·5†	+8000
20·6	25·6		+5·0			0

* The alteration of the zero was produced by the fields of the electromagnet and the exciting circuit.

† The change of sign of $d_2 - d_1$ in this and the two following experiments, for a direct field, is due to a reversal of the galvanometer terminals.

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
21·6	25·2		+3·6			0
19·6		23·5		+3·9	+0·45	−8000
19·7		23·8		+4·1		−8000
21·9	25·4		+3·5			0

Temperature 18·3° C.

March 19, 1912.—The cell was cleaned and refilled.

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.		$d_2 - d_1$.	H.
12·5	10·9		−1·6				0
12·6	10·8		−1·8				0
11·8		8·8		−3·0		−1·25	+14,000
11·7		8·6		−3·1			+14,000
12·0		9·1		−2·9	−2·95		+14,000
12·0		9·1		−2·9			+14,000
12·0		9·1		−2·9			+14,000

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.		$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
13·2	9·0		−4·2				0
13·1	9·1		−4·0	−4·13			0
13·0	8·8		−4·2			+1·43	0
10·9		8·2			−2·7		−14,000
10·9		7·5			−3·4	+0·73	−14,000

Temperature 18·7° C.

March 22, 1912.—The cell was cleaned and refilled.

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
15·7	15·7		0·0			0
15·9		14·7		−1·2	−1·25	+14,000
15·6	15·7		+0·1			0

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.		$d_2 - d_1$.	H.
17·6	17·6		0·0				0
16·4		17·7		+1·3		+0·9	−14,000
16·6		17·3		+0·7	+0·9		−14,000
16·6		17·2		+0·6			−14,000

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.		$d_2 - d_1$.	H.
17·5	17·3		−0·2				0
17·9		16·2		−1·7		−1·6	+14,000
17·9		16·1		−1·8	−1·8		+14,000
17·9		16·0		−1·9			+14,000

An examination of the tables given above shows that the approximate value of the deflection is 1 cm. for a field of 14,000 gauss. This value may be taken as indicating the true order of the effect. A calibration of the galvanometer showed that one scale division (*i.e.* 1 mm.) represented 5×10^{-11} ampère. The resistance of the cell between the transverse terminals was found to be 615 ohms and as that of the galvanometer is 16 ohms, the total resistance in the galvanometer circuit is 631 ohms. Hence 1 mm. on the scale represents $3{\cdot}15 \times 10^{-8}$ volt. A deflection of 1 cm. corresponds therefore to a transverse potential difference of $3{\cdot}15 \times 10^{-7}$ volt. The potential applied between the primary electrodes was 0·85 volt and as the distance between the electrodes is 1·5 cm., the primary potential gradient is 0·57 volt per centimetre. The distance between the transverse electrodes is 1·7 cm. From equation (1) we find, using these numbers, that the potential difference due to the true Hall effect will be $2{\cdot}17 \times 10^{-8}$ volt, while from equation (2) the accompanying Hall concentration effect will be $8{\cdot}15 \times 10^{-8}$ volt. This latter effect* is probably the one which has been measured, and the former, which would give rise to a deflection of one or two scale divisions, is included. These calculations are based on the assumption that the copper sulphate solution is completely dissociated, but whatever the extent of the dissociation the order of the calculated effect is the same as that of the experimental effect; for the function $\phi(c)$ is continuous and steadily increases with the concentration.

Although the large disturbing forces which gave rise to the effects observed by Bagard have been much reduced, there is still the possibility that the small effect in the present experiments may be due to a similar but far less effective cause. But if so, it is difficult to see how any effect due to arbitrary disturbances could give rise to such consistent results as those found. For not only was the liquid lamina changed for each experiment, the pole pieces were further apart in some cases than in others, and any erratic effect due to local disturbances would have had a good opportunity of showing itself, if it had existed. The effect observed appeared to grow for a short time but soon attained a steady value. It was impossible to observe the early stages of the deflection because several seconds were needed for the magnetic field to attain its steady value and on closing the galvanometer circuit a reading could be taken only after an additional 10 seconds had elapsed. When the magnetic

* It must be noted that in the calculation we have assumed that the solution is completely dissociated ($L = M = 1$). It can be shown that if $L \neq M \neq 1$, then $\frac{LV - MU}{L+M} > \frac{V-U}{2}$ because $V > U$. Hence the calculated value is too low. The solution contained 0·17 grm.-equivalent per litre, and was therefore by no means completely dissociated.

field was taken off, the deflection on closing the galvanometer circuit gradually became smaller.

At the suggestion of Sir Joseph Thomson, the following experiments were made on cells of copper sulphate gelatine in which movements of the solute as a whole are prevented. Drude and Nernst* have carried out experiments on gelatine laminæ, and they found that the large effect observed by the early experimenters did not exist. Their means of investigation was not delicate enough, however, and it seemed interesting to test the above experiments on liquid copper sulphate by examining a gelatine film of the same salt.

To a strong solution of copper sulphate, estimated by the iodine method and found to contain 83 grm. of copper sulphate per litre, was added sufficient gelatine to enable thin sections to be cut. The gel contained 8 per cent. of copper sulphate by weight. Two cells of the type (*b*) were constructed, and an experiment made with each. The potential difference between the primary electrodes was 38 volts. The following observations were taken:—

May 6, 1912.—Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
45·3	42·1		−3·2			0
45·3	42·1		−3·2			0
45·3	42·0		−3·3		+0·5	0
44·8		42·1		−2·7		+15,000
44·4		41·7		−2·7		+15,000
44·7	41·7		−3·0			0

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
45·1	42·5		−2·6			0
45·0	42·4		−2·6			0
44·7		41·7		−3·0	−0·5	−15,000
44·9		41·6		−3·3		−15,000
45·1	42·3		−2·8			0
45·0	42·4		−2·6			0

Temperature 17·6° C.

* 'Wiedemann Ann.,' 1891, vol. 42, p. 568.

May 7, 1912.—Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
40·0	25·6		−14·4			0
39·9	25·5		−14·4			0
39·9	25·6		−14·3			0
39·5		24·5		−15·0	−0·65	−15,000
39·9	25·6		−14·3			0

Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
39·9	26·0		−13·9			0
39·85	25·9		−13·95			0
39·8	25·9		−13·9			0
40·4		26·8		−13·6	+0·43	+15,000
39·9	25·9		−14·0			0
39·8	25·8		−14·2			0
39·8	25·6		−14·2			0

Temperature 17·5° C.

The thickness of the laminæ in the last two experiments was 30 μ. From the tables it is seen that a deflection of 5 mm. was found on applying a magnetic field of 15,000 gauss. This deflection disappeared within a minute from taking off the magnetic field. The sensitiveness of the galvanometer was tested and 1 mm. was found to correspond to $1·5 \times 10^{-10}$ ampère. The resistance of the lamina between the transverse electrodes was 2300 ohms, and therefore 1 mm. deflection corresponds to $3·5 \times 10^{-7}$ volt. Hence the magnitude of the transverse effect is $17·5 \times 10^{-7}$ volt. Using (1), where $\partial\pi/\partial x = 38/2·3 = 16·5$ volts per centimetre, H $= 15,000$ gauss, $z = 0·5$ cm., we find that the transverse potential difference is $19·8 \times 10^{-8}$ volt; while (2) gives a transverse potential difference of $7·4 \times 10^{-7}$ volt.

Experiments on (a) *Silver Nitrate Solution,* (b) *Cadmium Sulphate Solution.*—(*a*) A solution containing 10 per cent. of silver nitrate was used. This was contained in a cell made of mica, the inside dimensions of the cell being 2·6 cm. × 1·8 cm. × 0·05 cm. The primary electrodes were of silver, 0·05 cm. diameter; the transverse electrodes, also of silver, had a diameter 0·063 mm. The cell was mounted on a large sheet of mica which was fastened to one pole piece of the electromagnet.

The following readings were taken:—

May 25, 1912.—Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
30·3	27·6		−2·7			0
30·3	27·6		−2·7			0
30·6		28·5		−2·1		+14,800
30·6		29·0		−1·6		+14,800
30·6		29·1		−1·5	+1·0	+14,800
30·6		28·9		−1·7		+14,800
30·6		28·9		−1·7		+14,800
30·3	28·5		−1·8			0
30·3	28·5		−2·3			0

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
30·3	27·8		−2·5			0
30·3	27·8		−2·5			0
29·8		27·0		−2·8		−14,700
29·8		26·1		−3·7		−14,700
29·85		26·0		−3·85	−1·1	−14,700
29·9		26·0		−3·9		−14,700
29·85		26·1		−3·75		−14,700
29·85		26·1		−3·75		−14,700
30·3	26·9		−3·4			0

Temperature 18·6° C.

The deflection observed on applying a field of 14,800 gauss was 10 mm. The resistance of the cell between the transverse electrodes was 1200 ohms, and as 1 mm. deflection corresponded to $1·5 \times 10^{-10}$ ampère, the value of the transverse potential difference is $1·8 \times 10^{-7}$ volt. The primary potential gradient was 0·63 volt per centimetre, and the transverse electrodes were 2·1 cm. apart. From these data the calculated value* of the transverse potential difference, assuming it to be a Hall concentration effect, as represented by (2), is $1·24 \times 10^{-7}$ volt.

(*b*) A 15-per-cent. solution of cadmium sulphate was prepared. The dimensions of the cell were 1·4 cm. × 2·35 cm. × 0·09 cm., and the electrodes were of cadmium wire drawn out to convenient thicknesses, the diameter of the primary electrodes being 0·08 cm., that of the transverse electrodes 0·035 cm.

The following readings were taken :—

* The values of (V+U) for copper sulphate solution, silver nitrate solution, and cadmium sulphate solution are each equal to 12×10^{-4} cm./sec. for a potential gradient of 1 volt per cm.

October 23, 1912.—Field direct.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
26·5	26·1		−0·4			0
25·9		26·7		−0·8	+1·15	+11,400
26·5	26·2		−0·3			0

Field reversed.

z_1.	z_2.	z_3.	$d_1 = z_2 - z_1$.	$d_2 = z_3 - z_1$.	$d_2 - d_1$.	H.
26·5	28·2		+1·7			0
27·0		28·5		+1·5	−0·2*	−11,400
26·5	28·2		+1·7			0

Temperature 17·2° C.

* The unequal values of $(d_2 - d_1)$ are probably due to a small diffusion effect which would not reverse with the magnetic field.

The deflection obtained on applying a field of 11,400 gauss was 7 mm. The resistance between the transverse electrodes was 220 ohms and as 1 mm. deflection was found to correspond to $1·6 \times 10^{-10}$ ampère, the transverse potential difference is $3·52 \times 10^{-8}$ volt. The distance between the transverse electrodes was 2 cm. and between the primary electrodes 1·2 cm. and the primary voltage applied was 0·55. Using these data in (2), the calculated value of the transverse potential difference is $7·5 \times 10^{-8}$ volt.

Conclusion.

In the above experiments the Hall concentration effect contributes the greater part of the potential difference, and the true Hall effect, which would give rise to a deflection of 1 or 2 mm., is included. It was hoped at the outset that some information as to the nature of the process of reversal would be obtained by an examination of electrolytes whose differences of ionic velocities vary considerably. But the preponderance of the concentration effect, depending on the sum of the ionic velocities, has prevented this. Eight experiments have been made and all the potential differences are of the calculated order, they reverse with the magnetic field and act in the same direction, while the experimental conditions vary widely. These results are regarded as establishing the existence of a Hall effect in liquid electrolytes.

[*Note added January*, 1913.—The observations on copper sulphate solution are plotted in fig. 6. For low magnetic fields (8000 gauss) the error of

observation amounts to 20 per cent. of the total deflection. This error is attributed to disturbances in the cell. The point A departs from the linear relation by 27 per cent., while the point B is approximately 10 per cent. out. The points C and D correspond to a field of 14,000 gauss and the error of observation is smaller. The mean positions of the pairs of points A-B and C-D are marked ▲, and these lie approximately on a straight line passing

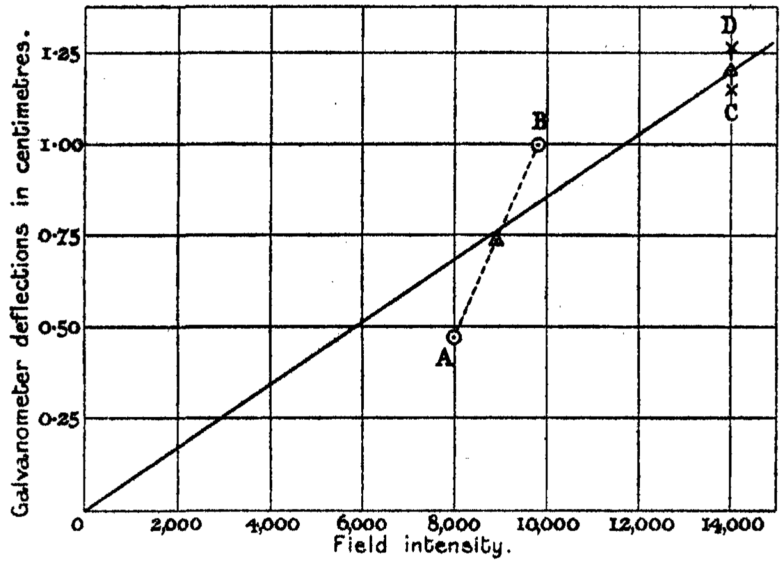

Fig. 6.

through the origin. Hence within the limits of experimental error the transverse potential difference is proportional to the magnetic field. It has been shown by Florio that the proportionality of the magnetic field and the large effect observed by Bagard may be due to the presence of vortical motions in the solution, and for this reason more reliance is placed on the uniformity of the effects observed and on the quantitative agreement with theory, in identifying the Hall effect, than on showing that a linear relationship exists between the magnetic field and the effect.]

The above experiments were made in the Cavendish Laboratory between October, 1911, and November, 1912.

I wish to express my indebtedness to Sir Joseph Thomson for advice and criticism during the progress of this research and to Mr. H. L. P. Jolly for the loan of the galvanometer.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

CONTENTS.

SAMUEL HAWKSLEY BURBURY, 1831–1911.

Mr. BURBURY was born at Kenilworth in May, 1831, and was educated at Shrewsbury School, where he gained the highest prizes for his studies. He subsequently entered at St. John's College, Cambridge, where he graduated in 1854 as fifteenth Wrangler and second Classic, having previously gained the Craven Scholarship (for Classics) as well as the Porson Prize.

About five years later he was called to the Bar, and it was not till about twenty years later that he commenced to specialise in mathematical science. He was elected a Fellow of the Royal Society in 1890.

His first substantial contribution, written in collaboration with the late Rev. H. W. Watson, Sc.D., F.R.S., was a treatise, published in 1899, on 'An Application of Generalised Co-ordinates to the Dynamics of a Material System.' The alliance with Watson was a successful one, for we find the same two writers bringing out 'The Mathematical Theory of Electricity and Magnetism,' in 1883–5, a book intended to give greater definiteness and precision to the deductive portions of the subject than was to be found in Clerk Maxwell's two volumes.

The first edition of Dr. Watson's 'Kinetic Theory of Gases' was published at the end of 1876, just three years before the first joint work with Burbury. The subject always appears to have had a fascination for Burbury. About the year 1890 mathematical physicists were turning their attention to the statistical molecular distribution commonly referred to as Maxwell's Law, and we find Burbury taking an active part in a controversy in which Boltzmann, Lord Kelvin, Lord Rayleigh, and several other physicists were involved. This controversy, briefly speaking, turned on the two questions, first, whether the Boltzmann-Maxwell distribution is always a possible one, and secondly, whether it can be proved to be the only possible one. It may perhaps be correct to say that the general result of these investigations has been to leave Maxwell's Law somewhat in a similar position to Euclid's eleventh axiom, a possible hypothesis, but not necessarily a unique one. Among Burbury's contributions at that time we notice papers—"Some Problems in the Kinetic Theory of Gases" ('Phil. Mag.,' Oct., 1890), and "The Collision of Elastic Bodies" ('Phil. Trans.,' 1891)—in the latter of which he criticises the test cases previously proposed by Lord Kelvin and Burnside, and proves that the conventional proofs of Maxwell's Law and Boltzmann's Minimum Theorem can be extended to doublets, lop-sided spheres, and systems of colliding rigid bodies generally. In a further paper ('Phil. Mag.,' Jan., 1894), Burbury extended the proof to groups of molecules under each other's influence, while subsequently ('Phil. Mag.,' June, 1894) he traced the relation between the law of distribution and the assumed property that dQ/T is a complete differential.

In these papers Burbury appears in the light of counsel for the defence, but when it comes to the question of proving the uniqueness of the Boltzmann-Maxwell distribution he takes up the opposite line, and shows that Boltzmann's Minimum Theorem, and the deductions following from it, are based on a certain assumption, which he calls "assumption A." This line of argument receives its fuller development in Burbury's treatise on 'The Kinetic Theory of Gases' published in 1899. As applied to collisions between two different kinds of molecules, the assumption is that the probability factor of a given distribution of co-ordinates and momenta between pairs of colliding molecules, previous to collision, is of the form Ff where F depends on the molecules of one kind and f on those of the other, in other words that the distributions of the two kinds, previously to collision, are independent of each other. This will no longer be true after the collisions have taken place, so that if F' and f' are the subsequent separate probability factors for the two systems, the probability factor for the combined system is not *really* $F'f'$. It thus becomes necessary to assume that between collisions a process of mixing takes place so that the distributions of the molecules which are *about* to collide again become independent and the new probability factor assumes the form $F'f'$. If assumption A be made, Burbury admits that Boltzmann's Minimum Theorem can be proved, but not otherwise. The question of reversibility has also been used by Burbury and others in this connection, who contend that for every motion which makes $Ff > F'f'$, as the result of a collision, an equally probable reversed motion must exist in which the opposite occurs.

In a letter to the present writer, dated December 17, 1901, Burbury says: "Now I say that the law has never been proved at all, except as a deduction from Boltzmann's assumption A. If it has ever been proved, or attempted, will you tell me where? Tait, Watson, Maxwell, Weinstein, all make Boltzmann's assumption. Further, there is no evidence whatever for Boltzmann's assumption, except that it leads to the law of equal partition. We are in a vicious circle. The tortoise is supported on the back of the elephant, and when I ask what the elephant is supported on they say it is suspended from the tortoise."

In his treatise Burbury considers the result of abandoning "assumption A." and making "assumption B," according to which "the chance of a given molecule having at any instant assigned velocities is not independent of the positions and velocities of other molecules at that instant." This leads him, at any rate for the simpler cases of elastic spheres, to a distribution in which the probability factor is an exponential function of an argument containing not only squares but also products of velocities. In other words, he finds that the velocities of neighbouring molecules become *correlated*. This would happen particularly in a dense medium, thus affording some theoretical explanation for the physical differences between such a medium and an ideal gas subject to Maxwell's Law.

From this time onwards, Burbury devoted a large amount of attention to

tracking and exposing assumption A, or its equivalent, in all the papers written on the kinetic theory. The late Willard Gibbs' 'Statistical Mechanics,' Jeans's papers, Planck's investigations, all fell under Burbury's critical eye; and it was not long before most writers found this part of their argument attacked in a short paper by Burbury.

One of the recent questions which attracted Burbury's critical mind was the loss of available energy accompanying the diffusion of two gases at constant volume, a subject dating back to a paper by Lord Rayleigh, published in 1876. Burbury's criticisms were published in the 'Phil. Mag.' for July, 1907, and in 'Science Progress.' The difficulty in the problem lies largely in the fact that it is impossible to assign a quantitative value to any irreversible transformation unless it is possible to restore the system to its original state by a compensating transformation, and further, unless the latter transformation is reversible, it is impossible to obtain a measure of anything but the sum total of the irreversible effects of the direct and reverse transformations. If there is one thing to be said in criticism of Burbury's views it is that he hardly appreciated—or if he did appreciate it he did not sufficiently emphasise the fact—that the whole question depends essentially on experimental evidence regarding the processes of separation of mixed gases. If we express the belief that the entropy of a gas mixture is the sum of the entropies of its components when each component occupies the same volume as the original mixture, this belief is founded on statements which experimental physicists give us and which they can only prove to be approximately true. If, however, we consider ideal perfect gases we find that this entropy property is independent of the other definitions of such a medium, just as Euclid's axiom of parallels is independent of the other axioms of geometry, and it is possible to formulate a theory of media the mixtures of which are defined as satisfying a different entropy property. Burbury frequently reverts to the argument, Why should two different gases behave differently to two different portions of the same gas?

Those who have entered into friendly controversies with Burbury on similar knotty points will well appreciate the zeal with which he would follow up a line of argument, till in many cases his opponent would have to give up the contest, often owing to lack of opportunity to continue it. He was a typical example of a school of mathematical physicists essentially characteristic of the second half of the nineteenth century. Most of his fellow workers have passed away, such as Maxwell, Kelvin, Boltzmann, Watson, Stoney, Willard Gibbs, all of whom devoted either the whole or a considerable part of their attention at one time or other to unravelling these difficult problems. Such work is usually described as theoretical. In reality it has every right to be called experimental. To find out what conclusions follow from certain assumed hypotheses is no less an experiment because it is conducted on paper instead of with apparatus.

For many years previous to his death Burbury suffered from deafness. Perhaps this was the reason for his abandoning his legal career and taking to

mathematical physics as a scientific recreation. He had four sons and two daughters. He died in August, 1911, and shortly afterwards one of his sons died when on active service in India.

It will be seen that Burbury's work consisted largely in an attempt to secure logical rigour of treatment in the branches of mathematical physics in which he was interested. It has certainly led to a closer examination of the foundations of statistical dynamics, and at the same time, when taken in conjunction with other contemporaneous investigations, has opened up a wide field of study which may well attract the attention of future workers.

G. H. B.

FREDERICK JOHN JERVIS-SMITH, 1848—1911.

THE REVEREND FREDERICK JOHN JERVIS-SMITH, the only son of the Reverend Prebendary Smith, of Taunton, was born at Taunton on April 2, 1848. He was educated at Pembroke College, Oxford. While still a boy at home he had the great advantage of meeting constantly William Ellis Metford, by whom his natural aptitude for science and mechanics was stimulated so that his genius, which was so marked in these directions, forced him at a later date to break away from the narrower life which his father wished him to follow. In obedience to this wish he entered the Church and acted for some years as his father's curate and organist, becoming later Vicar and Patron of the living of St. John's, Taunton. It must have been at this time also that with the help of Sir John Stainer he attained that knowledge of music and skill at the organ and piano that his friends so greatly admired, for a touch such as his could not have been acquired in later life.

While at Taunton he followed the bent that was so strong in him and carried on experimental work in his own workshop, acquiring by various means an intimate knowledge of workshop practice such as the amateur rarely possesses. In 1886 he was invited to take charge of the Millard Engineering Laboratory attached to Trinity College, Oxford, and it was here that his best work was done.

A good indication of the variety of Jervis-Smith's investigations may be found by reference to the 'Philosophical Magazine' in the twenty years from 1882 to 1902. The subject to which he devoted himself most particularly was that of work-measuring machines and integrators, and many of the papers are on this subject. Several papers refer to the measurement of the torsion of rotating shafts with a view to determine the power being trans-

mitted, and one of his early papers describes the means now adopted on large steamships, where, owing to the engines being turbines, indicated power cannot be ascertained and the torsional method is the only one available.

Other enquiries which interested him were the magnetic properties of metals as affected by mechanical stress or by heat; electric sparks and the influence on them of flame or pressure. Under this heading, probably, should be mentioned his beautiful electrically produced images of coins that he called inductoscript.

One of the most valuable results of Jervis-Smith's ingenuity and mechanical aptitude is his tram chronograph. Those who have used the old pendulum myographs so usual in physiological laboratories, where the time records are rendered tiresome by the variable speed of the recording surface, should be the first to appreciate this beautiful instrument, in which trouble from this cause is entirely eliminated. A still greater value has been given to this instrument by the perfection of the electromagnetic styles that he invented and made. By making his electromagnets extremely small and the yoke relatively short and thick he reduced the latent period so that this chronograph is now not only the most convenient but the most accurate instrument for ballistic and other measurements of the kind.

Other subjects of less interest perhaps in which Jervis-Smith made investigations or inventions were in relation to mercury pumps and means for raising the mercury continuously and automatically, quick distillation of mercury *in vacuo*, recalescence of iron, and high resistances made of graphite and plaster of Paris.

During the last few years since his retirement to his charming house near Lymington Jervis-Smith was greatly interested in glowing phenomena in vacuous bulbs moved or spun in electric and magnetic fields. On these he made numerous original experiments, but up to the present these results are not well understood.

Jervis-Smith was awarded a medal at the Paris Exhibition of 1878 for a dynamometer, and at the Inventions Exhibition at South Kensington he was awarded a silver medal for his work on dynamometers. He also received a medal from the Royal Humane Society for rescuing a person in danger of being drowned. He was a member of the Committee on Explosives appointed by the Home Office in 1895–96. He became a Fellow of the Royal Society in 1894.

He was keenly interested in the historical side of Physical Science, and often brought to light curious anticipations of more recent inventions. He found, for instance, that the telephone had been made and described in Italy as an instrument for recording taps upon it by movement at the receiving end. The former inventor had apparently invented the same instrument as Bell, but he never thought of speaking into it. This historical appreciation made the selection of Jervis-Smith to represent the University of Oxford at the tercentenary of Torricelli at Faenza in 1898 singularly appropriate.

Throughout his career one subject was constantly receiving his attention

and that was dynamometry in its widest sense. On this he had been collecting papers all his life, and in his later years he was putting these in order in the hope of seeing the great work completed which had gained so much from his originality. It is hoped that this will appear this year.

He married Annie Eyton, second daughter of T. Taylor, Esq., who with one surviving son remains to mourn his loss.

The singular charm, humour, and modesty of Jervis-Smith, no less than his genius, made his friendship a valued possession. The writer of this notice found in addition a community of taste and a mutual sympathy, and he has lost his closest and most valued friend and counsellor.

C. V. B.

JOHN BROWN, 1850—1911.

JOHN BROWN, who died on November 1, 1911, at his residence, Longhurst, Dunmurry, Belfast, was born close by, at Edenderry, in 1850, eldest son of John Shaw Brown, the proprietor and largely the developer of the well-known Edenderry flax spinning and weaving works. During the seventies of last century his father took a conspicuous and public-spirited part in social and political life in Ulster, several times contesting the Parliamentary representation of divisions of Belfast on moderate Liberal principles, as understood in those days. His son's interests from earliest years were mechanical and philosophical. After the usual school education at the Royal Academical Institution at Belfast, he went into the work of the firm. In his leisure time he kept in touch with the progress of physical science, largely through the correspondence columns of the 'English Mechanic,' a journal then at the zenith of its usefulness in keeping the workshop in touch with the laboratory, before the modern period when the rise of electric engineering has turned the professional societies into scientific institutions. In this way he made and retained the acquaintance of other practical mechanicians of scientific taste, some of whom have taken a notable part in subsequent developments.

In particular, he became fascinated, at a time when the primary battery was still a main electric source of power, with the problem of the seat of the transformation of the chemical into electric energy. Is the measured potential difference between copper and zinc due to a sudden transition between the metals where they are in contact, or is it mainly due to such transitions between each metal and the surrounding atmosphere in which the measuring apparatus must be immersed? The reasonings of Volta and

Faraday and Kelvin—necessarily general and somewhat vague up to the nineties because the existence and *rôle* of electrons as the agents of all electric change were still unrecognized—strongly fascinated him. Where the chemical affinity lay, there, as he thought, should the potential difference be, at any rate in the state of equilibrium when no current passes—for the passage of a current necessitates its own special distribution of driving force in accordance with Ohm's law, which must be brought about by the superposition of transient distributions of free charge on the intrinsic transitions of potential aforesaid. It was left to Brown to put these ideas to direct test: and the paper (1878) in which he announced that replacement of air or oxygen as the surrounding medium by sulphuretted hydrogen gas at once changed the direction of the potential difference between zinc and copper, attracted immediate attention and discussion. He became a refined and diligent experimenter in the field of voltaic combinations, stoutly adhering against all comers to the indications of Faraday, whom he took as his mentor (*cf.* obituary notice in 'Nature,' November 16, 1911), and encouraged by the interest and friendship of George FitzGerald, Oliver Lodge, J. D. Everett, and other friends and colleagues. When the resources, mostly self-constructed, of his own laboratory at Edenderry were inadequate, he worked for long spells in Everett's physical laboratory at the Queen's College, Belfast. At a later stage he was attracted to Trinity College, Dublin, to the laboratory of his friend FitzGerald; and while there, an explosion in chemical preparations, relating to his work on primary batteries, cost him the loss of an eye. Later he resumed similar work at Belfast. He had little instinct for publicity; yet during these years he produced, besides many local papers and lectures at Belfast, an extensive general experimental paper on contact electricity in 'Roy. Soc. Proc.,' and a later one in 1902 on the effect of a heated bath of petroleum in modifying this phenomenon. He seems to have been the first to publish the remarkable patterns produced by electric discharge on photographic plates.

He became interested also in the Hertzian electric waves, whose qualities were being explored and verified extensively in the Dublin laboratory by FitzGerald and Trouton and others about the time he was there—just as, later, the results of the introduction by Marconi of the aërial antenna, which was needed to effect the copious radiation necessary for telegraphic signalling, were first publicly verified by them at a regatta in Dublin Bay, as tested by the transmission of press messages to the shore.

On the introduction of internal combustion engines, Brown at once grasped the new possibilities which they brought, and he spent much time experimenting on the development of the motor car; but an isolated worker, far from the resources of capital and factories, could hardly much affect practical evolution in such a subject. He also worked on the development of a spring wheel to absorb shock. His experiences in this direction led him on to a cognate topic, on which he became a public force. The badness of the roads, especially in Ireland, was a main obstacle to the introduction of the new

type of locomotion. He invented an instrument, attachable to a car, to take a trace of the inequalities of the road; and he circulated the graphs thus obtained, to the occasional confusion of the road authorities. He pointed out the evils of the slipshod methods of road-repair, by loosely spreading macadam stones mixed with mud, that were then in vogue. He established the Irish Road Improvement Association, which brought pressure to bear on public bodies with considerable success, and later worked in touch with enlightened road engineers in Great Britain. In these ways he was a pioneer in a development which now, under Government direction, is producing fundamental improvement in the facilities for communications and for country life.

He grudged no time or effort to the stimulation of scientific interests in the community among whom he lived. He was one of the main forces which kept fresh and active in recent years the old-established Belfast Literary and Philosophical Society; and when the British Association last visited Belfast in 1902 he was the expert and indefatigable local Secretary of the meeting. He was elected a Fellow of the Royal Society in 1902.

J. L.

EDWARD DIVERS, 1837—1912.

EDWARD DIVERS, M.D., D.Sc., F.I.C., after an operation followed by a painful illness, died at his residence at Kensington on April 8. He was born in London on November 27, 1837, and therefore at the time of his decease had attained his 75th year. He was educated at the City of London School, the Royal College of Chemistry, and Queen's College, Galway. From this time onwards he was increasing his own knowledge, and by his numerous investigations added to that of others. In 1870 he received the appointment of Lecturer on Medical Jurisprudence at the Medical School of the Middlesex Hospital. The experience he gained whilst holding this position stood him in good stead in after life, and invested him with authority in connection with criminology. A great event in his career took place when he accepted a Professorship in Chemistry in the service of the Imperial Government of Japan. This was in 1873, at which time that country issued invitations to all nations that could give her assistance in acquiring the material civilisation of the West.

On his arrival in Japan, Divers had to attend to the building of his own laboratories, around which grew the palatial buildings of the Imperial College of Engineering. In 1882 he was appointed Principal of this

Institution. It was here, in consequence of an explosion in a test tube, that for some time he practically lost his sight. This, however, was partially regained, and, although with one eye he could read at a short distance from his face, he could not recognise acquaintances in the street. Notwithstanding this misfortune, contrary to expectations, Divers' power for work, rather than growing less, grew greater. Memoir followed memoir and paper followed paper. Many of these were written in conjunction with a colleague, an assistant, or some promising student. Amongst these the names of Haga, Takamine, Shimidzu, Nakamura and others will be familiar to many chemists. His work has appeared in the 'Transactions' and 'Proceedings' of the Royal Society, the 'Journal of the Chemical Society,' and particularly in the 'Journal of the College of Science of the Imperial University of Japan.' In the latter we notice papers on Mercury Sulphites, the Composition of *Tori mochi* or Japanese birdlime, Oxyamidosulphonates and their conversion into Hyponitrites, the Manufacture of Calomel in Japan, Sulphazotates, Sulphate of Hydroxylamine, Imidosulphites, Nitrilosulphates, and Sulphamide. In the 'Transactions of the Asiatic Society of Japan' we find contributions relating to Japanese meteorites and hot springs.

The accident which cut him off from pleasures which nearly all enjoy seems to have increased the time he had for original investigations. He gave himself but short holidays; and during the Long Vacation, when the halls of the College of Science were supposed to be deserted, the echo of a footstep or the hum of some quaint old melody told the intruder that Divers loved his laboratory better than hills he could not see. At the entrance to that college a large bronze bust reminds many in Japan of a teacher they admired.

He went to Japan with an engagement for five years; but he found an environment so fascinating and a bondage so agreeable, that he remained in that country without once leaving it for 26 years.

On his retirement he was made Emeritus Professor of the University of Japan, received the Second Class of the Order of the Sacred Treasure and the Third Class of the Rising Sun. On reaching England his activity continued. In 1902 he was President of the Chemical Section of the British Association. He also became President of the Society of Chemical Industry, and represented that Society on the governing body of the Imperial College of Science and Technology. In addition to these offices he was a Vice-President of the Chemical Society and of the Institute of Chemistry.

In 1865 he married Margaret Theresa FitzGerald, of Mayfield, County Cork. His only son, who joined the Chinese Customs service, succumbed to an illness in Amoy. His two daughters, the Comtesse de Labry and Mrs. Tilden, in common with all who knew him, mourn his loss. He had a genial and generous disposition, was full of humour, was always ready to give assistance or advice, and was esteemed by all. His high forehead and grey beard gave him a dignified appearance, while the kindly expression on his face was an invitation to friendship. He did very much more than any other

individual to found the present School of Chemistry in Japan, and his colleague, Professor Sakurai, writing from Japan, says Divers "will be for ever remembered in this country as the great promoter of chemical science."

J. M.

HENRY TAYLOR BOVEY, 1850—1912.

HENRY TAYLOR BOVEY was born at Torquay on March 7, 1850. He received his school education at Clevedon College, Northampton, a private school, many of whose pupils distinguished themselves afterwards at the University. A scholarship from this school carried him to Queens' College, Cambridge, where he read for the Mathematical Tripos. In those days it was considered necessary, if a man aimed at a high position among the Wranglers, to read during the whole of his three years with one of a few leading coaches, college and University lectures taking a secondary position. He became a pupil of W. H. Besant, F.R.S., of St. John's College, and graduated as Twelfth Wrangler in 1873, shortly afterwards being elected to a Fellowship at his college.

Deciding to become a civil engineer, he entered the office of Sir George Lister, who was at that time the engineer of the Mersey Docks and Harbour Board. He afterwards joined the staff of that Board as assistant engineer, in which capacity he had charge of some of the most important structures then in progress. It was, however, as a Professor of Engineering that Bovey was to make his mark. A severe accident in the football field, with broken ribs and a damaged lung, was the proximate cause of the change in his career. He was advised to spend some time in a dry climate, and this induced him to accept the offer of the Chair of Engineering at McGill College, Montreal, which was made to him at this time by Sir W. Dawson, and he went to Canada in the autumn of 1877 to take up this post. But at the end of the first year he appears to have been so dissatisfied with the organisation of the teaching that he sent in his resignation with the intention of returning to England. He was persuaded, however, by the Principal to reconsider his determination, and receiving from the latter a promise of support in a reorganisation of the department, he decided to remain. Although he did not know it at the time it was the opportunity of his life. In a few years the Engineering School at McGill was transformed. It became the leading institution of the kind on the American Continent, and his pupils were always sure of going straight from college into good engineering posts. But it was not by any means all plain

sailing. There were difficulties of organisation within, and the want of means to ensure development, until at last Sir W. Macdonald came to the rescue with princely donations. His first fight was to free his subject from the domination of the Arts Faculty, and to obtain recognition of an independent Faculty of Applied Science. In 1890 the Engineering building was begun, and he and the donor—Sir Wm. Macdonald—made a tour of Engineering schools in the States. From what they saw there it was easy to convince Sir William that McGill needed adequate buildings and Chairs for Physics and Chemistry, and Bovey's ideas of adequacy were wide and large.

One who knew him well writes: "He found a subordinate department of the Faculty of Arts. He freed it and made it a great Faculty. I think he did it first by reason of boundless energy. When he came over to the Imperial College he was already ill, and a mere shadow of himself, and could give no idea of what he was in the eighties and nineties. He was then sanguine and self-confident, and full of go. He had a real fund of geniality and kindness of heart. Everyone who came out was sure of a most kind welcome and helpfulness of every sort. He really had ideas that were worth while so far as the concrete creation of a great Faculty went, and from 1890 to 1900 he had practically a free hand. In working out his ideas another marked gift appeared. He always knew the right man to go to to get a thing done. He enjoyed meetings and remembered people, and had that mysterious way of knowing what was going on by instinct. His real gifts were practical organisation, knowing the right man, how to set about it, and no limit to what he wanted for the Faculty."

In 1907 an offer was made to him of the rectorship of the Imperial College of Science and Technology in London, and he was definitely appointed to it in May, 1908. But his health had commenced to break down before this, and after two years' work in the organisation of the new College, he resigned the post in December, 1909. He passed away at Eastbourne on February 2, 1912, and lies buried in Eastbourne Cemetery.

He married on May 5, 1880, Miss Emily Redpath, youngest daughter of Mr. John Redpath, of a well-known Montreal family. He is survived by his widow, two sons, and three daughters.

The Royal Society elected him a Fellow in 1902, and his old College in Cambridge conferred on him an honorary fellowship in 1906. He was one of the founders of the Canadian Society of Civil Engineers, and at one time or another held all the offices from Secretary to President. He was also one of the founders of the Liverpool Society of Civil Engineers. In 1896 he became President of Section III of the Royal Society of Canada. He was author of several text-books on Engineering.

W. M. H.

RIGHT HON. SIR JOHN CHARLES DALRYMPLE-HAY, BART., G.C.B., 1821—1912.

JOHN CHARLES DALRYMPLE-HAY, third baronet, was born in Edinburgh on February 11, 1821. He spent his early boyhood at home until sent to Rugby in 1833. Entering the Royal Navy in 1834, he joined H.M.S. "Thalia," serving in her on the West Coast of Africa. From 1839 to 1842 he served in H.M.S. "Benbow," on the Mediterranean Station, being present at the capture of St. Jean d'Acre by Sir Robert Stopford in 1840, and being gazetted for gallantry at the attack on Tortosa. Having passed his examination for Lieutenant in 1841, he attained that rank in 1844, and serving on the China Station became Flag Lieutenant to Admiral Sir Thomas Cochrane, who, in 1846, promoted him to a vacancy as commander of the "Wolverene."

Hay's next appointment was to H.M. Brig "Columbine," proceeding in her to the China Station in 1849. The opportunity now occurred for him to show the result of the excellent training he had received in ships commanded by able officers, animated by the great traditions of the Naval service. The Chinese coasts were infested by pirates, and it was by the squadron—two of which were paddle steamers—under Hay's command, that the most notable were destroyed in Bias Bay and the Tonquin River, places then uncharted and requiring great audacity and perseverance to navigate. It was here that the value of steam propulsion in war vessels came home to him. For this service he was promoted to Captain and presented by the merchants in China with a service of plate.

During 1846–50 Hay undertook observations in meteorology, and communicated to the Indian Government papers on the cyclone theory, remarks on three typhoons in the China seas, and on two hurricanes off Mauritius, besides papers on storms in the Atlantic off Bermuda and the Western Islands, neither of which appears to have been published.

After serving in H.M.S. "Hannibal" during the Crimean War he became Captain of H.M.S. "Indus," one of the last sailing line-of-battle ships commissioned for sea service, and on leaving her in 1859 his career at sea ended. This was not intentional on his part, for trusting to his long service and existing regulations he fully counted upon being given an Admiral's command.

But, being one of those officers of his day who appreciated the value of science when applied to his profession as a sailor, he saw an opening for utilising his energies in that direction for a time on land.

The construction of iron-built ships for war purposes which was attempted in the early forties was almost immediately discontinued as being quite unsuitable, and wood-built ships propelled by steam or sail, or both, as required, formed our Navy for several years. However, the use of iron as a valuable protection to wood-built floating batteries was shown by the

French when bombarding Kinburn in 1855. Then, in 1860, was launched the French wood-built armour-plated frigate "La Gloire," responded to in the same year by the British iron-built armour-plated frigate "Warrior." The latter vessel sounded the death-knell of the wood-built ship.

The early failure, and subsequent success and progressive use, of iron in the construction of warships when armour-plated had been favourably noted by Hay, enabling him to cast aside the strong predilection for the wood-built ship, which affected many able officers of his time, and he put all his strength into furthering what he considered to be the inevitable future.

In 1861 Hay became Chairman of the Iron-plate Committee appointed in 1860 to carry out experiments in armour and other proposals for introduction into the Navy. For this he had many qualifications, actual experience of the value of armour for ships during the Crimean war, considerable war service afloat, and a mind open to genuine improvements. Moreover, he possessed great tact and ability in smoothing the difficulties which presented themselves when presiding over a Committee consisting of eminent scientific members dealing with inventions and proposals, good, bad, or indifferent, often strongly pressed for adoption.

Following this, the Institution of Naval Architects elected him a Vice-President in 1862, and later on he became Chairman of the Millwall Shipbuilding Company, and also of Reuter's Telegraph Company.

The work he had so far undertaken was not enough for Hay's activities, for he sought other opportunities for promoting naval progress by entering Parliament. He was successively Member for Wakefield, 1862–65; Stamford, 1866–80; and Wigton Burghs, 1880–85.

In 1866 he accepted a seat on the Board of Admiralty, a post he held for two years and a half. It was during this period that Hay, now a Rear-Admiral, successfully contended for a large addition of armour-plated ships to the Navy, in spite of considerable opposition, even tendering his resignation of a coveted position rather than give way upon a question he considered vital to the strength of the Navy.

It was with deep regret that, at the age of 49, Sir John was obliged to relinquish all prospects of active service at sea. A new scheme of compulsory retirement for all officers who had been unemployed afloat for specified periods was ordered, and Hay, refusing the offer to be made an exception to the rule, had to go. If he could not serve his country in the way of his choice, he was, at any rate, free to do so in other directions. Thus, not only in Parliament, but at the meetings of the Institution of Naval Architects, he was a keen debater on naval questions, and he did good work as Vice-President of the Royal United Service Institution.

Of his published writings, the following may be mentioned: 1868, 'Lines from my Log Book'; 1876, 'The Flag List and its Prospects'; 1878, 'Ashanti and the Gold Coast'; 1883, 'Our Naval Deficiencies'; 1889, 'Piracy in the China Seas.' In 1903, when seismology was much to the front, he contributed to the 'Proceedings' an interesting paper, written from

his own naval experiences, "On Central American Earthquakes, particularly the Earthquake of 1838."

Sir John was the recipient of various distinctions. In 1852 he became a Fellow of the Royal Geographical Society, and in 1864 was elected a Fellow of the Royal Society. Ten years later he was appointed a Privy Councillor. Oxford and Glasgow conferred on him the honorary degrees of D.C.L. and LL.D. respectively. He was created K.C.B. in 1885 and G.C.B. in 1902.

Sir John married the Hon. Eliza Napier, third daughter of the eighth Lord Napier, in 1847, and by her had three sons and six daughters. She died in 1901. The eldest son having died in 1908, the next, William Archibald, succeeded to the baronetcy, which his father had held since 1861.

As a naval officer Hay was a strict disciplinarian, tempered with tact and full consideration for the welfare and happiness of those under his command, qualities fully appreciated by seamen. Both in private and public life he was remarkable for his genuine courtesy, coupled with the frankness of the sailor, and his memory will be long and warmly cherished by his acquaintances as well as friends, including many of the Fellows of the Royal Society, who much appreciated his regular attendance at the meetings and at other functions.

Admiral Sir John Charles Dalrymple-Hay died at his residence in London on January 28, 1912, in his 91st year.

E. W. C.

OSBORNE REYNOLDS, 1842—1912.

OSBORNE REYNOLDS was born August 23, 1842, at Belfast. He came of a clerical family. His grandfather and great-grandfather had been rectors of Debach-with-Boulge, Suffolk. His father, the Rev. Osborne Reynolds, was thirteenth Wrangler in 1837 (a year remarkable as being that of Green and Sylvester), and was subsequently Fellow of Queens' College, Principal of the Belfast Collegiate School, Headmaster of Dedham Grammar School, Essex, and finally, in his turn, rector of Debach.

For his early education Reynolds was indebted chiefly to his father, first at Dedham and afterwards privately. In 1861, at the age of nineteen, he entered the workshop of Mr. Edward Hayes, mechanical engineer, of Stony Stratford, in order, as Mr. Hayes expressed it, "to learn in the shortest time possible how work should be done, and, as far as time would permit, to be made a working mechanic before going to Cambridge to work for Honours."

The motives which guided the first steps in Reynolds' career may be stated in his own words.* "From my earliest recollection I have had an irresistible liking for mechanics; and the studies to which I have specially devoted my time have been mechanics, and the physical laws on which mechanics as a science are based. In my boyhood I had the advantage of the constant guidance of my father, also a lover of mechanics, and a man of no mean attainments in mathematics and their application to physics." After referring to the year he spent with Mr. Hayes, he proceeds:—"Having now sufficiently mastered the details of the workshops, and my attention at the same time being drawn to various mechanical phenomena, for the explanation of which I discovered that a knowledge of mathematics was essential, I entered at Queens' College, Cambridge, for the purpose of going through the University course, previously to going into the office of a civil engineer." The decision to proceed to Cambridge appears to have been taken rather suddenly, for his previous education had not included Greek; he succeeded, however, by the obstinate labour of a few weeks, in reaching the standard of the "Previous Examination." His mathematical studies were pursued with success, for he graduated in 1867 as seventh Wrangler, and was immediately afterwards elected to a Fellowship. He then entered the office of Mr. John Lawson, civil engineer, of London. In 1868 he was elected to the newly instituted professorship of engineering in the Owens College.

This professorship was almost† the first of its kind in England, although similar chairs had existed for some time in Scotland and in Ireland, and had been illustrated by such names as those of James Thomson and Rankine. It is possible that Reynolds was influenced to some extent by

* Taken from his letter of application for the Owens College professorship.

† Fleeming Jenkin had been appointed professor of civil engineering at University College, London, in 1865.

the tradition of these chairs. With Rankine, at all events, for whom he always professed the greatest admiration, he had strong affinities, in the range of his scientific interests, in the directness of his intuitions, and in the courage and tenacity with which he attacked difficult and complicated problems. He resembled Rankine also in his views as to the scientific character of the training to be given to engineering students. The course of instruction which he arranged for his pupils, and to which he consistently adhered, was remarkable for the thoroughness and completeness of the theoretical groundwork. On one point he was uncompromising. In his mind all engineering was one, so far as the student is concerned, and the same fundamental training was required whatever the nature of the specialisation which was to come afterwards in practice. As an ideal principle this can hardly be gainsaid, although the varied ramifications of mechanical science, and the increasing multiplicity of "subjects," have in more recent times compelled a deviation from it. The course laid out by Reynolds was no doubt felt by many students to be severe, and there is testimony that his lectures were not always easy to follow. It is therefore hardly to be wondered at if at first some shade of disappointment was felt by the eminent practical engineers, and other friends of the Owens College, who had worked for the creation of the professorship. Few could have foreseen at that time how splendidly the appointment was destined to be justified, not only by the distinguished scientific career for which it served as a base, but also by the succession of students who derived stimulus and inspiration from the genius of their teacher, and who came afterwards to occupy important positions in the professional as well as in the academical world. Both branches of his activity were greatly assisted by the establishment of the Whitworth Engineering Laboratory in 1888, although some facilities for hydrodynamical experiments on a moderate scale had been secured at an earlier date. Several of the more important appliances in the new laboratory, *e.g.* the triple-expansion engines and the hydraulic brakes, were specially designed by Reynolds for purposes of study and research, and presented many novel features.

Shortly after his appointment Reynolds entered on the career of original research which continued without interruption down to his retirement in 1905. The results of many of his investigations were communicated in the first instance to the Manchester Literary and Philosophical Society, which cherished the memory of Dalton, and was still distinguished by the presence of Joule. In the affairs of this Society Reynolds took a lively interest; he was Secretary from 1874 to 1883, and President for the term 1888–9. After the death of Joule he wrote for the Society a memorial volume, which was published in 1892; and he was the leading spirit in the movement for a public monument to Joule, which resulted in the beautiful statue by Gilbert which now adorns the Manchester Town Hall.

His scientific writings are a remarkable fulfilment of the plan traced out in the letter which has been quoted. They deal almost entirely with mechanical

questions, or with physical phenomena so far as these appear to be susceptible of mechanical interpretation. Although they treat of subjects which are at first sight widely different in character, there are many underlying affinities, and trains of thought which constantly recur. It is characteristic of Reynolds that, even when they bear on questions of immediate practical import, there is a persistent endeavour to penetrate to fundamental principles, and to disregard what is accidental or adventitious. It is probably for this reason, in part, that there was some delay in the recognition of his work by the practical world, even in cases where his ideas have since been proved to contain the germ of fruitful applications. His work on turbine pumps, for example, is now recognised as having laid the foundation of the great modern development in these appliances, whilst his early investigations on the laws governing the condensation of steam on metal surfaces, and on the communication of heat between a metal surface and a fluid in contact with it, stand in a similar relation to recent improvements in boiler and condenser design.

About the year 1899 the Cambridge University Press suggested to Reynolds that a collected edition of his papers would be valuable, and offered to undertake the publication. This signal compliment on the part of his old University was greatly appreciated by him, and in due course two considerable volumes appeared. Some idea of the extent of his scientific activity may be gathered from an inspection of the list of contents of this edition. In the way of practical papers, we find, in addition to those already referred to, investigations on the "racing" of the screws of steamers, on the steering of screw steamers, on rolling friction, on the errors of indicator diagrams, and on the action of tidal currents in the silting of estuaries. These, and others, may still be read with profit, and display, equally with the more impressive contributions to science, his skill in unravelling and explaining a mass of complicated detail by the light of some simple mechanical principle.

In the scientific world at large, however, the reputation of Reynolds is most likely to rest in the future on his contributions to general physics, and, in particular, to hydrodynamics, although here also the suggestion came usually from some practical question of engineering. The paper on "Lubrication" (1886), for example, explains on familiar hydrodynamical principles how the presence of a film of oil is maintained between a rotating shaft and its bearings, in spite of enormous pressures between them. The explanation, when given, is almost obvious; but Reynolds was the first to formulate it explicitly, and to submit it to the test of calculation. To many minds it had not even occurred that there was anything to be explained at all.

In the paper "On the Law of Resistance in Parallel Channels" (1883), an experimental investigation is made of the circumstances which determine whether the flow of water through a pipe shall be smooth and regular, with a resistance varying as the velocity, as in Poiseuille's experiments with capillary tubes, or irregular and sinuous (or "turbulent," to use Lord Kelvin's happy

description), with a resistance varying more nearly as the square of the velocity, as in most questions of practical hydraulics. The conclusion, based on the dynamical principle of "dimensions," and confirmed by the experiments, is that there is a certain "critical velocity," depending on the ratio of the (kinematic) viscosity of the fluid to the diameter of the pipe, at or about which the transition takes place from one type of motion to the other. The character of the motion, at any stage, was revealed by the behaviour of a filament of coloured water introduced into the stream, a device often used by Reynolds in the study of fluid motion. The experiments described in the paper, and often repeated by Reynolds in his lectures, were of a beautiful and striking character. Although much has since been written on the subject, and something still remains to be cleared up, the investigation has taken rank as a classic, and is perhaps the most widely appreciated amongst the decisive achievements of the author.

The most extensive piece of purely experimental work carried out by Reynolds was undoubtedly that bearing on the Mechanical Equivalent of Heat, and described in the Bakerian Lecture for 1897. This was prompted by a number of considerations. The original determination of Joule depended ultimately on the properties of a particular thermometer. More recent observers had endeavoured to refer their measurements to the absolute scale, but with somewhat discordant results. Measurements of the heat generated in the hydraulic brakes in the Whitworth Laboratory had been conducted under Reynolds' direction for some years, and compared with the work absorbed, but this had been done mainly by way of verification, and for practice. He was at length led to recognise that he had at his command appliances which could be used on an unprecedented scale, and to solve a more definite problem. The question which he attacked was to ascertain the total amount of work required to raise a pound of water from freezing point to boiling point, or in other words, the *mean* specific heat (in terms of work) between these two temperatures. The object of the measurement thus became absolutely definite, and independent of any arbitrary thermometric scale; and at the same time, owing to the great quantities which could be dealt with, the margin of error could be greatly reduced. The principle of the method was simple in the extreme; water was fed into the brake at the freezing temperature, there raised by friction to boiling point, and then carried off to a tank on the table of a weighing machine. The work absorbed was given by the couple on the brake, multiplied by the total rotation of the shaft. A good deal of preliminary work was required, and some improvements in the mechanism, before the method was brought to its ultimate degree of accuracy. The final measurements, which extended over a considerable period, were undertaken by Mr. W. H. Moorby. The definitive result was that the mean specific heat between freezing and boiling points, expressed in mechanical units, at Manchester, is 776·94. The whole investigation is a model of scientific method, and may claim to rank among the classical determinations of physical constants.

Among the shorter writings which have played a part in the development of science mention may be made of the papers on the "Refraction of Sound" (1874), and on "Group-Velocity of Waves" (1877). The effect of wind on the transmission of sound had been discussed by Stokes in 1857. Reynolds independently gave the same explanation, and confirmed it by a series of experiments; he also added an examination of the various effects of a vertical temperature gradient, according as the temperature decreases or increases upwards. As regards group-velocity, a geometrical explanation had been given by Stokes, but Reynolds brought in the very important and significant fact that the group-velocity gives also the rate of *transmission of energy*.

A word must be said as to the style and composition of his papers, if only because these elements have been the occasion of some injustice and neglect. The leading idea is in nearly all cases simple; his bias was, indeed, always to look for a simple explanation of a phenomenon, rather than to frame a theory based on the concurrence of a number of independent causes. But when he came to write out the results of his researches, he appears to have aimed in the first place at a statement which should accurately reflect his own experience of the matter. Unfortunately, the points which have given most trouble to the author are not always those which are most difficult to the reader, and *vice versâ*. When, on one or two occasions, he took up a subject for a second time, with a view to explaining it to a popular audience, he was lucid and forcible. Like some other distinguished physicists whom one can call to mind, he was not a great reader of contemporary scientific literature. When new theories were brought under his notice, he thought the questions out independently and in his own way. He held to his own technical terms and phrases, even when there was an established usage, and sometimes employed familiar terms in a new sense. Consequently, the reader of his papers will at times find it necessary to bring some patience to the task, if he means to extract the solid value which is to be found in them. But, with one or two exceptions, there are no cases of obscurity which cannot be surmounted in this way.

Although he sometimes affected, not quite seriously, to despise mathematics, he had considerable mathematical power, and did not hesitate to apply it on occasion. One or two of his calculations, if isolated from their context, would rank as considerable analytical achievements, even if they had been carried out with the help of modern and more expeditious methods. Reference may here be made to the paper on "Dimensional Properties of Matter in the Gaseous State" (1879), and to that on the "Dynamical Theory of Incompressible Viscous Fluids" (1894). The former paper, written in the early days of the radiometer, is important in relation to the theory of gases, and discusses, both experimentally and mathematically, the new phenomenon of "thermal transpiration." In the latter an attack is made on the very difficult problem of calculating theoretically the critical velocity, already referred to, at which the regular flow of a liquid through a pipe becomes unstable.

At the British Association meeting of 1885, Reynolds read a short paper on the "Dilatancy" of granular media. When an agglomeration of loose granules is closely packed, it cannot have its shape altered without increasing, at all events temporarily, the volume of the interstices. Consequently, if such an aggregation is prevented from expanding, it becomes rigid. These principles were illustrated by simple but striking experiments, and it was also pointed out that they lead at once to the explanation of a familiar but hitherto obscure phenomenon, viz. that when a foot is planted on the firm moist sand of the sea-shore, the space immediately around becomes relatively dry, whilst the space beneath the foot, when this is raised, is found to be abnormally wet. This explanation, it may be mentioned, gave great delight to Lord Kelvin. In spite of the interest of the experiments, Reynolds was careful to state that the theory was anterior to them. He had long speculated on the possibility of a mechanical theory of matter and ether which should, amongst other things, resolve the riddle of gravitation. He had convinced himself that a medium composed of smooth rigid grains (*e.g.* spheres) in contact was promising, and it was by reflection on the properties of such a medium that he was led to foresee the somewhat paradoxical behaviour of sand and other granular aggregations which was so beautifully confirmed by his experiments.

The results of the remarkable physical speculation referred to are recorded in the long memoir on the "Sub-mechanics of the Universe" which marked the close of his scientific career. This was read before the Royal Society on February 3, 1902, and now constitutes the third and final volume of his collected papers. Unfortunately, illness had already begun gravely to impair his powers of expression, and the memoir as it stands is affected with omissions and discontinuities which render it unusually difficult to follow. No one who has studied the work of Reynolds can doubt that it embodies ideas of great value, as well as of striking originality; but it is to be feared that their significance will hardly be appreciated until some future investigator, treading a parallel path, recognises them with the true sympathy of genius, and puts them in their proper light.

Prof. Reynolds, owing to the failing state of his health, withdrew from the active work of his chair in 1905. His last years were spent in retirement at Watchet, Somerset, where he died on February 21, 1912. He had been twice married; first, in June, 1868, to a daughter of Dr. Chadwick, of Leeds, who died in July, 1869; and secondly, in December, 1881, to a daughter of the Rev. H. Wilkinson. A son by the first marriage died in 1879. By his second marriage he leaves three sons and a daughter.

The character of Reynolds was, like his writings, strongly individual. He was conscious of the value of his work, but was content to leave it to the mature judgment of the scientific world. For advertisement he had no taste; and undue pretensions on the part of others only elicited a tolerant smile. To his pupils he was most generous in the opportunities for valuable work which he put in their way, and in the share of credit which he assigned to them in cases of co-operation. Somewhat reserved in serious or personal

matters, and occasionally combative and tenacious in debate, he was in the ordinary relations of life the most kindly and genial of companions. He had a keen sense of humour, and delighted in starting paradoxes, which he would maintain, half seriously and half playfully, with astonishing ingenuity and resource. The illness which at length compelled his retirement was felt as a grievous personal calamity by his pupils, his colleagues, and by other friends throughout the country.

He was elected a Fellow of the Royal Society in 1877, and received a Royal Medal in 1888. He was made an Honorary Fellow of Queens' College, Cambridge, in 1881, and received the degree of LL.D. from the University of Glasgow in 1884. An admirable portrait by Collier, presented by scientific friends and admirers from all parts of the kingdom, hangs in the hall of the Manchester University.

H. L.

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END OF THE EIGHTY-EIGHTH VOLUME (SERIES A).

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ERRATA, ETC.

Page 231. In column headed "Mean of 1883–1884,"

For 7·449 *read* 7·499.

Page 254. Paper by E. W. MARCHANT.

Reference to following paper should have been made :—

Ottavio Bonazzi, "Misura della Permeabilità del Ferro nel Campo Magnetico delle Scariche Oscillatorie," 'Pubbl. del Ist. Fis. del Univ. di Pisa,' 1910.

Page i. Obituary Notice of S. H. BURBURY—Line 10,

For 1899 *read* 1879.

Date of issue.	Date of issue.	Date of issue.